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INVESTIGATION OF THE REGULARITIES OF THE ALKYLATION OF XYLENES WITH PROPYLENE IN THE PRESENCE OF $BF_3 \cdot H_3PO_4$

The alkylation of *o*-, *m*-, and *n*-xylenes with propylene in the presence of $BF_3 \cdot H_3PO_4$ is a simple and convenient route for the synthesis of mono- and diisopropylxylenes, by oxidation of which derivatives of benzoic acid and phthalide, benzenepolycarboxylic acids, phenols, ketones, and other interesting substances can be obtained ([1]). In addition, the study of this process provides useful material for establishing the basic regularities of the formation of polyalkylbenzenes. The propylation of *m*- and *n*-xylenes in the presence of $BF_3 \cdot P_2O_5$ and of *m*-xylene in the presence of $BF_3 \cdot H_3PO_4$ was studied by Kirklend and co-workers ([2]); however, these authors did not examine the regularities of the reaction and were unable to obtain isopropylxylenes in yields above 52%.

Table 1

Hydrocarbon	B.p., °C	M.p., °C	n_D^{20}	d_4^{20}
o-Xylene	144.5	–	1.5055	0.8806
m-Xylene	139.0	–	1.4971	0.8642
n-Xylene	138.4	13.2	1.4958	0.8611
4-Isopropyl-*o*-xylene	199.5	–	1.5096	0.8713
3-Isopropyl-*o*-xylene	204.5	–	1.5102	0.8940
4-Isopropyl-*m*-xylene	197.8	–	1.5013	0.8770
5-Isopropyl-*m*-xylene	194.6	–	1.4950	0.8606
2-Isopropyl-*n*-xylene	196.0	–	1.5010	0.8762
4,5-Diisopropyl-*o*-xylene	239.5	–	1.5015	0.8809
4,6-Diisopropyl-*m*-xylene	236.0	16.5	1.4980	0.8720
2,5-Diisopropyl-*n*-xylene	244.0	37.4	–	–

In the present work a systematic study was carried out of the influence of catalyst concentration, temperature, reaction time, and molar ratio of the reactants on the yield and composition of the alkylation products of *o*-xylene (I), *m*-xylene (II), and *n*-xylene (III). Conditions were found that make it possible to obtain isopropylxylenes in yields of about 90% of theory; the relative reactivities of xylenes and isopropylxylenes were established, and the kinetic features of the reaction were elucidated. Alkylation and distillation of the catalyst were carried out by the previous method (^{3}).

Determination of the composition of the alkylates showed that propylation of (I) gives 4-isopropyl-*o*-xylene (IV), 3-isopropyl-*o*-xylene (V), and 4,5-diisopropyl-*o*-xylene (VI); (II) gives 4-isopropyl-*m*-xylene (VII), 5-isopropyl-*m*-xylene (VIII), 2-isopropyl-*m*-xylene (IX), 4,6-diisopropyl-*m*-xylene (X), and 2,5-diisopropyl-*m*-xylene (XI). The monoalkylate of (III) consists exclusively of 2-isopropyl-*n*-xylene (XII), while the dialkylate consists predominantly of 2,5-diisopropyl-*n*-xylene (XIII). The isomers were separated by repeated rectification on a column of 45-50 theoretical plates; (X) and (XIII) were purified by freezing out and recrystallization. The principal constants of the compounds obtained and the characteristics of the initial xylenes, given in Table 1, agree with data (^{2}, ^{4}). Hydrocarbons (V) and (VI) have not been described in the literature.

The composition of the isomers was established by oxidation to benzenepolycarboxylic acids, refractometrically, and with the aid of infrared absorption spectra. The first method was used mainly for identification of the reaction products and for "semiquantitative" determination of the percentage composition of the isomers; the second, for rapid determination of relative

quantities (IV) and (V), (VII) and (VIII) (the difference in the refractive indices of the isomers made it possible to establish concentrations with an accuracy of 2-5%).

The separation of benzenetricarboxylic acids was based on the fact that, upon methylation, trimesic acid, unlike hemimellitic and trimellitic acids, gives liquid trimethyl trimesate, which is easily separated from the high-melting trimethyl esters and is soluble in the form of 1,3-dimethyl hemimellitate. The esters were identified by their melting points and converted by hydrolysis into the corresponding acids. Trimellitic acid (the oxidation product of (IV), (VII), and (IX)) had m.p. 228-234° (with decomposition), hemimellitic acid 193-196° (with decomposition), and its dimethyl ester 149°; trimethyl and triethyl trimesates melted at 144 and 133.5°, which corresponds to the data of (5). Mixed samples of the indicated substances with known pure preparations gave no depression of the melting point.

Isopropylxylenes were oxidized to benzenetricarboxylic acids with nitric acid in an autoclave at 200° for 8-10 hr. To obtain tribasic acids as the main product (yield 80-95%), it is necessary to take, per 1 part by weight of hydrocarbon, 45 parts of 20-25% HNO_3. Under milder conditions it is possible to carry out incomplete oxidation of the hydrocarbons. For example, (IV), on boiling with an excess of 10% HNO_3 (atmospheric pressure), is converted in 45-53% yield into 3,4-dimethylbenzoic acid (m.p. 166°), and with 25% HNO_3 into a mixture of methylbenzenedicarboxylic acids. Isopropylxylenes (V), (VII), and (IX) are oxidized by 10-15% HNO_3 in an autoclave at 180° for 3 hr to trimellitic acid (30-40%) and dimethylphthalidcarboxylic acids (56-60%). The latter were also obtained by oxidation of the hydrocarbons with alkaline $KMnO_4$ (yield 25%) and trimethylphthalides (1). By the combined action of nitric acid and an alkaline solution of $KMnO_4$ we succeeded in oxidizing (VI), (X), and (XIII) to pyromellitic acid (m.p. 276-280°; tetramethyl ester m.p. 142°) in only 20-23% yield, since the reaction stopped at the formation of a mixture of incomplete oxidation products or, under severe conditions, the substance was completely destroyed.

Oxidation of (XIII) in an autoclave gave the dilactone of 2,5-di-(α-hydroxyisopropyl)terephthalic acid, which sublimes without decomposition at 325° (yield 8%). We were unable to obtain benzene-1,2,3,5-tetracarboxylic acid; the presence in diisopropyl-*m*-xylenes, along with (X), of 1,2,3,5-tetraalkylbenzene present in the mixture in an amount of 80-90% was demonstrated by spectral analysis. Isopropylxylenes were also identified by autoxidation. Thus, (IV) was oxidized by atmospheric oxygen with 3 mg/mole of manganese resinate at 110° for 4 hr to a hydroperoxide concentration of 21%. Decomposition of the hydroperoxides with conc. H_2SO_4 gave, in 64% yield, 3,4-dimethylphenol with m.p. 62.5°, 3,4-dimethylphenoxyacetic acid with m.p. 162°, and acetone (2,4-dinitrophenylhydrazone with m.p. 125°). Other autoxidation products were described by us earlier (1).

The results of some experiments on the propylation of xylenes are summarized in Table 2, where, for clarity, in addition to the composition of the reaction mass and the yields of products, the apparent ratios of the rate constants for the alkylation of isopropylxylenes and the starting xylene ($r = k_2/k_1$) and the actual extents of alkylation are indicated. The values of r and q were determined from the formulas

$$q = M + 2D, \qquad M = (U^r - U)/(1 - r), \tag{1}$$

where U, M, and D are, respectively, the molar fractions of xylene, mono- and diisopropylxylenes in the catalyzate (6).

From the data of Table 2 it is evident that an increase in the temperature and concentration of $BF_3 \cdot H_3PO_4$ promotes a decrease in the relative rate of formation of secondary alkylation products. This regularity, first observed by one of us jointly with Kurashev and Pushkin in the case of alkylation of benzene with propylene (7), is probably characteristic of all

Table 2*

No.	$BF_3 \cdot H_3PO_4$ taken, per 1 mol xylene	Propylene taken, per 1 mol xylene	$q \cdot 100$	$T_{\text{react.}}$, °C	Feed rate of propylene, h^{-1}	Xylenes, mol.%	Isopropylxylenes, mol.%	Isopropylxylenes, % of theory	Diisopropylxylenes, mol.%	Diisopropylxylenes, % of theory	r	1,2,4	1,2,3	1,3,5
1	2,5	50	42,0	60	10	61,6	34,8	69,6	3,6	14,4	0,38	75	25	–
2	5,0	52	50,8	60	15	53,1	43,0	82,7	3,9	15,0	0,25	80	20	–
3	7,5	51	50,4	60	20	52,7	44,2	86,5	3,1	12,3	0,19	–	–	–
4	10	50	49,7	60	25	52,9	44,5	89,0	2,6	10,4	0,17	85	15	–
5	20	50	49,6	60	25	52,8	44,8	89,6	2,4	9,6	0,16	88	12	–
6	10	60	49,4	20	15	57,4	35,8	59,7	6,8	22,6	0,59	60	40	–
7	10	51	50,5	40	20	53,0	43,5	85,3	3,5	13,7	0,22	–	–	–
8	10	51	50,8	50	25	52,2	44,8	87,9	3,0	11,8	0,18	–	–	–
9	10	50	49,7	80	25	52,7	44,9	84,8	2,4	9,6	0,15	96	4	–
10	10	60	56,8	60	40	48,2	46,8	78,0	5,0	16,6	0,25	80	20	–
11	10	60	50,9	60	60	55,3	38,5	64,2	6,2	20,7	0,41	65	35	–
12	10	80	79,0	60	10	30,2	60,6	75,7	9,2	23,0	0,20	76	24	–
13	10	33	33,0	60	20	68,1	30,8	93,3	1,1	6,6	0,17	–	–	–
14	10	31	30,4	60	20	70,9	27,8	89,9	1,3	8,4	0,26	68	2	30
15	10	78	76,5	60	25	33,4	56,7	72,7	9,9	25,4	0,25	65	2	33
16	10	65	61,0	20	15	50,0	39,0	60,0	11	33,8	0,62	70	2	28
17	10	30	27,4	50	15	73,6	25,4	84,6	1,0	6,7	0,27	100	–	–
18	10	50	39,9	20	10	65,1	29,9	59,8	5,0	20,0	0,60	100	–	–
19	10	30	29,2	80	15	72,0	26,8	89,3	1,2	8,0	0,25	100	–	–
20	10	40	39,6	60	10	62,9	34,6	86,5	2,5	12,5	0,26	100	–	–

* In experiments 1–13 the addition of *o*-xylene was studied, in 14–16 that of *m*-xylene, and in 17–20 that of *p*-xylene.

processes of alkylation of aromatic hydrocarbons with olefins in the presence of $BF_3 \cdot H_3PO_4$. As is readily shown with the aid of the equation $\lg(r_{T_1}/r_{T_2})/\lg(r_{T_1}/r_{T_3}) = T_3(T_2 - T_1)/T_2(T_3 - T_1)$, which follows elementarily from the Arrhenius equation (r_{T_i} is the ratio k_2/k_1 at absolute temperature T_i), the effect of temperature on the magnitude of r has a more complex character than might have been expected. For example, if $r_{293} = 0.6$, and $r_{323} = 0.27$, then r_{353} should be 0.15, which does not correspond to reality, since the values of r at 50 and 80° are practically equal.

Temperature and, still more, the concentration of the catalyst should not exert a strong influence on the true ratio of the rate constants for alkylation of xylene and isopropylxylene (^{3}). The indicated regularity also cannot be explained by the dealkylation of diisopropylxylenes: the rate of this process is too low (at 60

–80° $K = 0.005$—0.008 h^{-1}).

There is reason to believe that in the present case the situation is generally simple. When the reaction conditions do not ensure a high rate of addition of the olefin to the aromatic hydrocarbon, the concentration of the alkylating agent in the reaction zone will increase, tending toward a certain limiting value, and this will promote both polymerization of the olefin and the formation of products of alkylation of aromatic hydrocarbons by polymers, as well as the secondary alkylation reaction (see the experiments at a high propylene feed rate). And indeed, at low temperature and insufficient catalyst concentration, not only is much "polyalkylbenzene" always formed, but considerable polymerization of the olefin also takes place. As the reaction conditions are improved, the values of r rapidly approach the true ratio of the rate constants for alkylation of isopropylxylenes and xylene, ultimately becoming⋯

a practically constant value. The data of Table 2 and Fig. 1 convincingly show that, under favorable conditions, the alkylation of xylenes proceeds as a quasi-halogen irreversible consecutive reaction.

In studying the influence of various factors on the isomer ratios, it was noted that (IV) and (VIII) are formed not only directly through attack at the corresponding position of the xylene ring, but also as a result of isomerization of (V) and (VII). Many investigators, beginning with Jacobsen and Apschütz [8] and up to the present [9], have explained isomerization reactions

Fig. 1. Alkylation of xylenes with propylene at 60° in the presence of 0.1 g-mol/mol $BF_3 \cdot H_3PO_4$. The curves were calculated from equations (I). In the alkylation of *o*-xylene $k_2/k_1 = 0.17$, and in the alkylation of *m*- and *p*-xylenes $k_2/k_1 = 0.25$. *a*, *b*, and *c* denote, respectively, the experimental amounts of the alkylation products of *o*-xylene (M_o, D_o), and of *m*- and *p*-xylenes ($M_{m,p}, D_{m,p}$).

(including the abnormal formation of 1,3-, 1,3,5-forms) by dealkylation of polyalkylbenzenes. However, our experimental data cannot be explained by this theory, since with $BF_3 \cdot H_3PO_4$ the rate of isomerization exceeds the rate of dealkylation by tens and hundreds of times. For example, at 80°, (V) is converted so rapidly into (IV) that after only 4-5 h even spectral analysis cannot establish the presence of the starting hydrocarbon in the isomerizate. At 60—80°, (VII) isomerizes into (VIII) in 20 h to approximately 98%. In both cases, the disproportionation products of isopropylxylenes are formed in an amount not exceeding 1%. 1,2,4-Triisopropylbenzene and 1,2,3,5-dimethyldiisopropylbenzenes, except for (XI), undergo isomerization very readily. Dialkylbenzenes are converted into the *m*-isomers very slowly, while hydrocarbons (IV), (VI), and (VIII)—(XIII) do not change at all under the action of $BF_3 \cdot H_3PO_4$. On the basis of these facts, the regularities of the isomerization of polyalkylbenzenes can be formulated as follows: migration of the isopropyl group is intramolecular in character and occurs mainly when alkyl radicals are present in the 2,3; 2,4; or 2,3,5 positions relative to it.

At 20–25° isomerization of the hydrocarbons practically does not occur; migration of the methyl radical does not take place even at 100°. All the regularities described above make it possible not only to explain the nature of substituent orientation—for example, the reason for the formation, during propylation of (VIII), of a mixture of (XI) and (X), etc.—but also indicate a way to control the process in order to obtain the desired substances in maximum yield.

The reaction of alkylation of xylenes with propylene in the presence of $BF_3 \cdot H_3PO_4$ can be recommended for preparative syntheses of (IV), (VI), (VIII), (XII), (XIII), and possibly even (V), since, when a good column is available, separation of (IV) and (V) is easily achieved.

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