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INTERPHASE INTERACTION OF STYRENE WITH FORMALDEHYDE CATALYZED BY ORGANIC SULFONIC ACIDS

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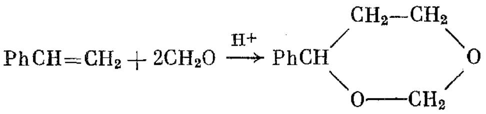
Catalysis involving interphase transfer in reactions accelerated by acids [1] can also occur in the acid-catalyzed reaction of an olefin with formaldehyde (I) via the Prins reaction to give 1,3-dioxane (or a 1,3-diol), which usually takes place in a two-phase system [2]. In the presence of H_2SO_4 the process occurs primarily in the aqueous phase containing the catalyst [3].

According to [4], C_{11}–C_{18} alkanesulfonic acids and long-chain N-alkylaminobenzene- and naphthalenesulfonic acids catalyze the reaction of isobutylene with I in a two-phase system.

In the present research, in the case of the acid-catalyzed reaction of styrene (II) with I, we investigate the effectiveness of the action of organic sulfonic acids as catalysts of the Prins reaction in order to ascertain some answer as to whether organic sulfonic acids are catalysts of interphase-transfer reactions.

We selected this reaction as a model reaction because of the fact that it proceeds under mild conditions and selectively [3]: The only product is 4-phenyl-1,3-dioxane (III)



We chose toluenesulfonic acid (TSA), the Petrov catalyst (PC), and synthetic alkylbenzenesulfonic acids (ABSA) with various molecular masses as the catalysts. The activities of the organic sulfonic acids in the reaction were expressed by the magnitudes of the relative catalytic effectiveness (RCE).

DISCUSSION OF RESULTS

It is apparent from Table 1 that the specific rate of the reaction in the presence of H_2SO_4 over the range of concentration from 0.045 to 2.0 g-eq/liter is $(18.0 \pm 3)\cdot10^{-3}$ mole/min·g-eq. Toluenesulfonic acid (TSA) is a more active catalyst than H_2SO_4. In a 0.6 N solution of TSA the rate of the process exceeds that observed for H_2SO_4 and is $69\cdot10^{-3}$ mole/min·g-eq; the RCE is 3.8. When the TSA concentration is increased to 1.0 N, the reaction rate increased to $125\cdot10^{-3}$ mole/min·g-eq, $\tau/2$ is 12 min, the yield of III reaches 90%, and the RCE is 7.

The PC displayed high activity in the Prins reaction: At a concentration of 0.17 N the rate of the process was $48.8\cdot10^{-3}$ mole/min·g-eq and the RCE was 2.7; at a concentration of 0.35 N, $W_{sp} = 86.0\cdot10^{-3}$ mole/min·g-eq, and the RCE increased to 4.8.

The most interesting results were obtained when ABSA with different lyophilicities were used (see Table 1). All of the tested ABSA have high catalystic activity, and their specific catalytic activities (based on one SO_3H group) far exceed the activity observed for H_2SO_4. In the presence of 0.33 N ABSA-300 the reaction rate exceeds the rate of reaction with the participation of H_2SO_4 by a factor of three; the RCE in this case was 9. We found that ABSA-440 proved to be an even more effective catalyst of the Prins reaction. The maximum RCE values are observed over the range of low ABSA concentration. At ABSA concentrations from 0.045 to 0.125 N the RCE value reaches 33.

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In the case of the simultaneous use of an organic acid and H_2SO_4 the introduction of an ABSA leads to a substantial increase in the catalytic action of H_2SO_4, and RCE = 5 (Table 2).

A number of experiments were carried out with a mixture of II and ethylbenzene (IV) in order to ascertain the effect of dilution of the olefin on the reaction rate and the RCE value. It is apparent from Table 3 that, in the presence of IV, the rate of the reaction catalyzed by H_2SO_4 decreased significantly: $W_{sp} = 3 \cdot 10^{-3}$ mole/min•g-eq, as compared with $W_{sp} = 18.0 \cdot 10^{-3}$ mole/min•g-eq without IV (see Table 1). In experiments with ABSA-440 the W_{in} values (the initial rates) were also somewhat lower; however, the RCE values increase and reach 92.5-113.6 (see Table 3). When the reaction is carried out with a mixture of 1 N H_2SO_4 and 0.25 N ABSA-440, the RCE reaches 33.3 (see Table 3), which is higher by a factor of six than in the absence of IV (see Table 2).

Inasmuch as the reaction of II with I proceeds in a two-phase system, one might think that the high catalytic activities of organic sulfonic acids are achieved through acceleration of mass transfer as a consequence of an increase in the size of the interface between the organic and aqueous phase. In order to check this assumption we carried out a series of experiments using nonionogenic surfactants (Table 4), which are good emulsifiers. Their addition to the reaction system leads to persistent foam formation during the course of carrying out the experiments. A comparison of the data obtained (see Tables 1 and 4) shows that the introduction, into the reaction mixture containing a 1 N H_2SO_4 solution, of 1-10% by mass of nonionogenic surfactants of various types does not accelerate the reaction.

One might assume that the greater effectiveness of the action of ABSA as compared with H_2SO_4 is associated with the specific distribution of the reagents and the catalyst in the two-phase system. In order to shed some light on this problem we studied the distribution of the reaction components between the organic and aqueous phases. It is apparent from Table 5 that when one uses H_2SO_4, TSA, ABSA-300, the catalyst remains primarily in the aqueous phase. In the case of ABSA-440 (which is soluble in both oils and water), the ABSA-440 passes into the organic phase to the degree of 44%. Formaldehyde is found primarily in the aqueous solution, and its percentage in the organic phase increases (5.9-8.4%) in the presence of an ABSA.

TABLE 1. Condensation of II with I

Catalyst	Concn., g-eq/liter	$W_{in} \cdot 10^3$, moles/liter·min	$W_{sp} \cdot 10^3$, moles/min·g-eq	τ/2, min	Yield of phenyldioxane, %	RCE
H_2SO_4	0,045–2,0	3,8–53,0	18,0±3	240–22	59–97	–
TSA	0,25	15,1	60	90	63	3,3
"	0,60	41,5	69	35	85	3,8
"	1,00	125,0	125	12	90	7,0
PC	0,17	8,3	48,8	–	30	2,7
	0,35	30,0	86,0	55	82	4,8
ABSA-300	0,33	53,5	162	27	90	9,0
ABSA-440	0,0455	26,7	593	68	64	33,0
"	0,125	75,0	600	23	89	33,0
"	0,25	93,8	375	14	95	21,0
ABSA-500	0,20	37,5	187	40	96	10,0
ABSA-550	0,18	93,4	430	18	91	24,0

TABLE 2. Catalytic Action of the 1 N H_2SO_4—Organic Sulfonic Acid System

Organic sulfonic acid	Concn., g-eq/liter	$W_{in}^{X+H_2SO_4} \cdot 10^3$, moles/liter·min	$W_{sp}^{X+H_2SO_4} \cdot 10^3$, moles/min·g-eq	τ /2, min	Yield of phenyldioxane, %	RCE
PC	0,17	37,5	32	38	93	1,8
ABSA-300	0,33	125,0	94	11	100	5,2
ABSA-440	0,25	125,0	100	11	100	5,5
ABSA-500	0,20	107,0	89	11	93	4,9
ABSA-550	0,18	107,0	90	15	94	5,0

TABLE 3. Condensation of II Diluted with IV (molar ratio 1:1) with I

Catalyst, g-eq/liter		$W_{in}\cdot 10^3$, moles/liter·min	$W_{sp}\cdot 10^3$, moles/min·g-eq	τ/2, min	Yield of III, %	RCE
ABSA-440	H_2SO_4					
–	1,0	3,0	3,0	–	22	–
0,045	–	12,5	277,7	68	74	92,5
0,125	–	25,2	201,6	23	89	67,2
0,25	–	85,2	340,8	18	100	113,6
0,25	1,0	125,0	100,0	15	96	33,3

TABLE 4. Effect of the Addition of Nonionogenic Surfactants on the Rate of Condensation of II with I in the Presence of 1 N H_2SO_4

Nonionogenic surfactant	Surfactant concn., %	τ/2, min	Reaction time, min	$W_{in}\cdot 10^3$, moles/liter·min	Yield of phenyldioxane, %
DE-2	1	54	120	25	74
"	10	57	180	19	80
Proxamine-204	1	60	180	20	81
"	10	62	180	25	85
Diproxamine-157	1	62	180	22	86
"	10	75	180	21	83

TABLE 5. Distribution of the Catalyst (acid) and Substrates I and II at 25°C between the Aqueous and Organic Phases in the Following System: 10 ml of Formalin, 0.1 mole of I, 3 ml (0.025 mole) of II, and the Catalyst (acid)

Catalyst, g-eq/liter	Relative amt., %					
	Acids		Formaldehyde		Styrene	
	Phase					
	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic
H_2SO_4, 1.0	99,5	0,5	95,5	4,5	0,7	99,3
TSA, 0.31	98,1	1,9	95,8	4,2	3,0	97,0
ABSA-300, 0.17	97,0	3,0	91,6	8,4	63,6	36,4
ABSA-440, 0.12	56,0	44,0	94,1	5,9	56,3	47,6

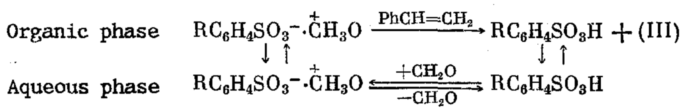
The distribution of styrene between the aqueous and organic phases changes substantially as a function of the nature of the catalyst. In the case of the use of H_2SO_4 and TSA the olefin is found primarily in the organic phase (97.0-99.3%).

In the presence of an ABSA more than half of the olefin used in the reaction passes into the aqueous phase. The aqueous phases that contain the ABSA remain turbid even after prolonged standing. It is known [5] that the solubility of styrene in water is extremely low (0.08% by mass). The high percentage of the olefin in the aqueous layer in the presence of an ABSA is probably due to the formation of a colloidal system rather than to an increase in its solubility.

In order to ascertain the effect of the solubility of the olefin in the aqueous phase on the course of the process we carried out a series of experiments in which we added 5 and 10 ml of p-dioxane to the starting reaction mixture (10 ml of formalin, 3 ml of styrene, and 0.5 g of H_2SO_4). After stirring for 2 h at 25°C and subsequent standing of the reaction mixture, we obtained transparent aqueous and organic layers. The solubility of styrene in the aqueous layer increased from 0.7% by mass to 19.7 and 38.0% by mass, respectively. The rate of the process (see Table 1 for the conditions) in the case of the addition of p-dioxane was $W_{in} = 10\cdot 10^{-3}$ mole/liter·min (in the absence of p-dioxane $W_{in} = 8\cdot 10^{-3}$ mole/liter·min). Consequently, a 25-fold to 50-fold increase in the olefin concentration in the aqueous phase did not lead to a substantial acceleration of the reaction of styrene with formaldehyde. In the case of complete homogenization of the reaction system (by the addition of 60 ml of p-dioxane) the reaction rate also changed slightly and amounted to $W_{in} = 8.6 \cdot 10^{-3}$ mole/liter·min. A similar phenomenon was observed in experiments with p-dioxane when ABSA-440 was used as the catalyst.

Thus it follows from the results that we obtained that the catalytic action of ABSA in the Prins reaction is not associated with an increase in the interphase area (experiments with nonionogenic surfactants) or an increase in the olefin concentration in the aqueous layer (experiments with p-dioxane). The high catalytic activity of the ABSA is evidently explained by the fact that when they are present, the process takes place primarily in the organic phase.

On the basis of the experimental data it may be assumed that the accelerating action of ABSA in the Prins reaction is due to the phenomenon of interphase transfer [6, 7] as a consequence of the formation of a formaldehyde—ABSA ion pair via the scheme



$$\begin{tikzcd}
\text{Organic phase} & RC_6H_4SO_3^-\cdot\overset{+}{C}H_3O \arrow[r, "PhCH{=}CH_2"] \arrow[d, shift right] & RC_6H_4SO_3H + (III) \arrow[d, shift right] \\
\text{Aqueous phase} & RC_6H_4SO_3^-\cdot\overset{+}{C}H_3O \arrow[u, shift right] \arrow[r, shift left, "+CH_2O"] & RC_6H_4SO_3H \arrow[u, shift right] \arrow[l, shift left, "-CH_2O"]
\end{tikzcd}$$

The possibility of the occurrence of the reaction in the organic phase was confirmed experimentally. Thus III is formed in ~90% yield in the reaction of paraformaldehyde (solid phase) with II in the presence of ABSA-440 (without water) under similar conditions (90°C, formaldehyde:styrene ratio = 2.5:1) after 90 min. This reaction does not take place under the influence of concentrated H_2SO_4.

EXPERIMENTAL

For our experiments we used 37% aqueous solutions of I, II, and IV with 98-99% purities [according to the results of gas—liquid chromatography (GLC)], cp grade 98% H_2SO_4, and commercial cp grade TSA, as well as the PC in the form of the industrial product (molecular mass of the sulfonic acids = 290), which was a mixture of organic sulfonic acids obtained by sulfonation of the kerosene or gasoline distillate; the percentage of sulfo groups was 24.8%. Elementary analysis: C 43.5; H 8.4; S 9.8%. The average chain length was C_{10}. The ABSA were products of sulfonation of alkylbenzenes with molecular masses from 300 to 550. The degree of sulfonation was 76-90%. The average lengths of the alkyl chains were as follows: C_{10} for water-soluble ABSA-300, C_{17} for water-oil-soluble ABSA-440, and C_{24} and C_{28}, respectively, for oil-soluble ABSA-500 and ABSA-550. The nonionogenic surfactants were DE-2, proxamine-204, and diproxamine-157 (block copolymer of ethylene oxide and propylene) [8].

The condensation of II with I (molar ratio II:I = 1:4) was carried out at 90°C in a glass thermostated apparatus of the long-necked flask type with a volume of 50 ml set up on high-speed oscillator. Into the test we introduced 0.5 moles (6 ml) II and 0.2 moles I (20 ml of formalin).

Beforehand, we established that the rate of the reaction of II with I in the presence of H_2SO_4 and organic sulfonic acids does not depend on the degree of stirring within the limits of 100 to 600 rpm. The experiments were carried out at 150-200 rpm. Samples that were neutralized with K_2CO_3 were collected by means of a syringe in the course of the experiments. The percentage of I was determined in the lower aqueous layer by the oxime method. The upper oily layer was analyzed by GLC for the percentage of III and the unchanged II (with decane as the standard). Analysis by GLC was carried out with an LKhM-8MD chromatograph with a 1-m long column; the liquid phase was SE-30 (10%), the carrier was Chromosorb W (60-80 mesh), and the programmed rise in temperature (25°C/min) ranged from 50°C to 250°C.

According to the data in [2, 4], the condensation of the olefin with I in 1,3-dioxane in the presence of H_2SO_4 proceeds in the aqueous layer, and the process is a second-order reaction, whereas in the case of an excess amount of one of the components the equation follows a pseudofirst-order equation.

The rate of the reaction was judged from the magnitude of the initial rate (W_{in}, mole/liter·min), the transformation of II, and the formation of III, which was determined graphically. The action of the organic catalysts was characterized by the RCE value:

$$\mathrm{RCE} = W^{x}_{sp}/W^{H_2SO_4}_{sp}$$

where W^{x}_{sp} and $W^{H_2SO_4}_{sp}$ are the specific reaction rates (in moles per minute per gram equivalent of the acid) at identical temperatures and starting concentrations of the reagents in the presence of organic sulfonic acids (X) and H_2SO_4 calculated from the expressions

$$W^{x}_{sp} = W^{x}_{in}/C_{x}, \quad W^{H_2SO_4}_{sp} = W^{H_2SO_4}_{in}/C_{H_2SO_4}$$

where C_x and $C_{H_2SO_4}$ are the concentrations of the catalysts in gram equivalents per liter.

In the case of the simultaneous use of H_2SO_4 and organic sulfonic acids the RCE values were calculated from the formula

$$\mathrm{RCE} = \frac{W^{x+H_2SO_4}_{sp}}{W^{H_2SO_4}_{sp}}, \quad W^{x+H_2SO_4}_{sp} = \frac{W^{x+H_2SO_4}_{in}}{C_x + C_{H_2SO_4}}$$

where $W^{x+H_2SO_4}_{in}$ and $W^{x+H_2SO_4}_{sp}$ are, respectively, the initial and specific rates of the reaction that takes place in the presence of a mixture of H_2SO_4 and the organic sulfonic acid.

The calculations of the RCE values were made without allowance for the acidity functions of the solutions: The determination of these functions by spectrophotometry was hindered as a consequence of the dark color of the starting ABSA.

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CONCLUSIONS

1. Aromatic sulfonic acids are active catalysts in the reaction of styrene with formaldehyde, a reaction that proceeds in a two-phase system; their specific catalytic activity (based on one SO_3H group) exceeds by far the activity of sulfuric acid.

2. The catalytic action of alkylbenzenesulfonic acids (ABSA) in the Prins reaction depends on their lyophilicity. Water-soluble ABSA-300 is less active than water–oil-soluble ABSA-440 and oil-soluble ABSA-500 and ABSA-550. The maximum catalytic effect of ABSA-440 is observed when the reaction is carried out with styrene diluted with ethylbenzene.

3. It was demonstrated experimentally that, in the presence of alkylbenzenesulfonic acids, the process takes place primarily in the organic phase.

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