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CONCLUSIONS

1. The thermal decomposition of furazane in the gas phase proceeds by a biradical mechanism with the nonsynchronous cleavage of the N-O and C-C bonds in the ring.

2. The gas-phase monomolecular cyclodecomposition of furoxane is facilitated by 4-6 kcal/mole and proceeds by a concerted mechanism.

LITERATURE CITED

- 1. R. Pearson, Symmetry Rules in Chemical Reactions [Russian translation], Izd. Mir, Moscow (1979), pp. 403-406.
- 2. V. G. Prokudin, G. M. Nazin, and G. B. Manelis, Dokl. Akad. Nauk SSSR, 225, 917 (1980).
- 3. V. D. Kolosov, M. K. Orlova, G. A. Osipov, Yu. A. Pankrushev, G. K. Klimenko, and

V. I. Slovetskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1057 (1976).

SULFO CATION-EXCHANGE RESINS AS HETEROGENEOUS CATALYSTS FOR THE REACTION

OF STYRENE WITH FORMALDEHYDE

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K. A. Kasymova, V. Z. Sharf, E. F. Litvin, and E. N. Grigor'eva

Sulfo cation-exchange resins (SC) are catalysts for the condensation of olefins with formaldehyde (Prins reaction) [1]. This reaction in the presence of SC presumably proceeds by a carbonium ion mechanism by analogy to that found in aqueous mineral acids [2]. According to Delmas and Gaset [3], the catalytic activity of SC in the Prins reaction is superior to that of H_2SO_4 (relative to equimolar amounts of SO_3H groups).

In the present work, we studied the dependence of the activity of macroporous and gel SC on their structure and composition for the model reaction of styrene (I) with formaldehyde (II) to form 4-phenyl-1,3-dioxane (III)

$$PhCH=CH_{2}+2CH_{2}O \xrightarrow{R-} SO_{3}H Ph-CH O O CH_{2}$$

where R is the polymer matrix. The activity of the cation-exchange resins was characterized by the initial reaction rate (W_0) .

RESULTS AND DISCUSSION

Table 1 shows that various macroporous ion-exchange resins differ in their static exchange capacity (SEC) by not more than a factor of 2, while the value for W_0 ranges from $0.72 \cdot 10^{-3}$ to $5.76 \cdot 10^{-3}$ mole/g·min and the yield of (III) ranges from 15 to 97% depending on the structure and dispersion of the SC. The value for W_0 increases in the series: levatite S-100 < KU-23 (10/60) < KRS-40t with increasing content of crosslinking agent (divinylben-zene (DVB)).

Grinding macroporous SC leads to an increase in their catalytic activity by a factor of 2-4.7 (see Table 1). The dependence of W_0 on the SC particle size indicates that the reaction proceeds in the intradiffusion region [4]. The catalytic activity of gel SC is characterized by W_0 from $1.6 \cdot 10^{-3}$ to $4.16 \cdot 10^{-3}$ mole/g·min. We should note that in the case of KRS-type SC, the catalyst activity is virtually independent of the extent of crosslinking upon increasing the DVB content from 1 to 40%. In contrast to macroporous SC, the activity of gel samples does not change markedly with change in particle size. An exception is found for the KRS-12p cation-exchange resin.

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TABLE 1. Condensation of (I) and (II) in the Presence of Sulfo Cation-Exchange Resins

· · ·	ί	[1	
Ion-exchange resin	DVB con- tent, %	SEC, mg- eq/g	₩ ₀ ·10 ³ , mole/g· min		Yield of (III),%	
			frac- tion 1*	frac- tion 2*	frac- tion 1	frac- tion 2
Maçroporous						
KU-23 10/60 KRS-40t KRS-30t-11 Amberlist-15 Vofatite U-39 Levatite S-100	10 40 30 - - 8	4.5 3.3 3.1 5.1 2.6 3.6	$\begin{array}{c} 2.20 \\ 2.22 \\ 1.48 \\ 1.38 \\ 0.86 \\ 0.72 \end{array}$	5,76 5,00 2,32 5,42 2,08 3,36	45 58 35 32 27 15	87 75 67 67 97 69
KRS-10 KRS-12p KRS-40p KRS-40p-11 Amberlite IR-120	1 12 40 40 8	Ge1 5,0 3,9 3,8 2,6 3,4	2,96 2,60 3,92 2,22 1,60	2.74 4.16 2.80 1.80 2.00	66 48 61 44 37	55 71 65 42 53

*Fraction 1: particle size for KRS-40t, amberlist-15, vofatite U-39, and levatite-100 from 0.25 to 1.0 mm, for KU-23 and KRS-30t-11 from 0.32 to 1.25 mm. For gel SC from 0.5 to 1.0 mm except for KRS-1p (from 0.25 to 0.5 mm). Fraction 2: SC with 0.1 mm particle size.

Comparison of the SEC and W_0 data of macroporous and gel SC shows that no correlation is found between these two indices. This apparently occurs because not all the sulfo groups participate in the catalysis. The macroporous and gel SC tested are efficient catalysts for the Prins reaction. Greatest activity is found for KU-23 and vofatite U-39; the yields of (III) after 2 h were 87 and 97%, respectively.

This reaction system contains three phases: 1) the organic phase containing (I) and (III), 2) the aqueous phase (solution of (II)), and 3) solid SC. The reaction of (I) and (II) occurs on the surface of macroporous SC and in the bulk of the SC phase in the case of gel forms. Apparently, an ion pair $R - \sum_{SO_3^-} CH_3O$, is formed in the reaction of (I) with a SO₃H group, in which $R - \sum_{SO_3^-} SO_3^-$ is the anion of the ion-exchange resin. The reaction of the $R - \sum_{SO_3^-} CH_3O$ ion pair with (I) leads to the formation of (III) and the regeneration of the acid group of the catalyst.

Delmas and Gaset [3] attributed the high activity of SC to the presence of hydrophilic SO_3H groups and hydrophobic aromatic rings of the polymer hydrocarbon framework, which facilitate the adsorption of (I) and (II), respectively.

According to Rys and Steinegger [5], the sulfonic acid groups in the SC have high acidity which, in particular, for amberlist-15 in water corresponds to the acidity function H_0 for 36-37% H_2SO_4 . Apparently, this factor primarily accounts for the high efficiency of the action of SC in the Prins reaction.

EXPERIMENTAL

The cation-exchange resins were sulfonated copolymers of styrene and divinylbenzene.

Macroporous cation-exchange resins: KU-23 10/60 (the numerator gives the mass fraction of DVB in the copolymer, %, and the denominator give the volume fraction of the pore-forming agent). KRS-40t and KRS-30t-11 are active cation-exchange resins sulfonated by chlorosulfonic acid with DVB as the crosslinking agent (up to 90% para and up to 10% meta isomers). Amberlist-15, vofatite U-39 and levatite-100 are commercial products.

Gel cation-exchange resins: KRS-lp, KRS-l2p, KRS-40p, and KRS-40p-ll (activated sulfonated cation-exchange resins; the numbers give the extent of crosslinking and n is the DVB p-isomer), and amberlite R-l20. The sulfo cation-exchange resins were initially converted to the H⁺ form. The SEC was found according to Saldadze and Kopylova-Valova [6]. <u>Reagents.</u> The sample of styrene (I) was freshly distilled (99% purity). A chemically pure grade sample of ethylbenzene was used. A 36% solution of (II) was prepared by heating paraformaldehyde at reflux in water for 8-10 h.

The condensation of 3 ml (I) with 10 ml formalin was carried out in a thermostatted apparatus [7] with stirring at 300-400 cycles per min. The (I):(II) mole ratio was l:4. The reaction was carried out with 5% ion-exchange resin at 90°C for 2 h. Under these conditions, the reaction rate did not increase with an increase in the oscillation rate. The reaction products were analyzed by gas-liquid chromatography [7]. The value for W₀ was determined graphically at styrene conversion up to 20%. The experiments were carried out after initial maintenance of the ion-exchange resin in the working solution of (II) until swelling of the catalyst was complete.

CONCLUSIONS

1. Macroporous and gel sulfo cation-exchange resins are active catalysts for the condensation of styrene with formaldehyde. The product, 4-phenyl-1,3-dioxane was obtained in up to 97% yield.

2. The activity of macroporous sulfo cation-exchange resins increases with decreasing particle diameter but in the case of the gel samples, granule size has only a slight effect on the reaction rate.

3. The enhanced activity of sulfo cation-exchange resins is presumably a result of the high value of the acidity function H_0 of the sulfonic acid groups of the cation-exchange resin.

LITERATURE CITED

- J. Maurin and E. Weisgang, Bull. Soc. Chim. France, 3080 (1964); B. N. Bobylev, E. P. Tepenitsyna, and M. I. Farberov, Kinet. Katal., <u>10</u>, 151 (1969); V. I. Isagulyants and M. G. Safarov, Zh. Prikl. Khim., <u>39</u>, 1148 (1966).
- 2. E. Erendale and L. A. Mikeszka, Usp. Khim., 23, 223 (1954).
- 3. M. Delmas and A. Gaset, Tetrahedron Lett., 22, 723 (1981).
- 4. N. G. Polyanskii, Catalysis by Ion-Exchange Resins [in Russian], Izd. Khimiya, Moscow (1973), p. 29.
- 5. P. Rys and W. Steinegger, J. Am. Chem. Soc., 101, 4801 (1979).
- 6. K. M. Saldadze and V. D. Kopylova-Valova, Complex-Forming Ion-Exchange Resins [in Russian], Izd. Khimiya, Moscow (1980).
- V. Z. Sharf, E. F. Litvin, K. A. Kasymova, and V. A. Afans'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 1463 (1985).