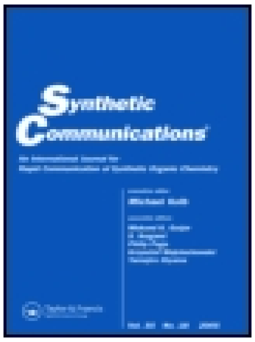

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POLYMERS AS REAGENTS AND CATALYSTS. PART 28. THE EFFECT OF POLYMER CATALYST STRUCTURE ON THE ESTERIFICATION OF ACIDS*

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Summary - Crosslinked sulphonated polystyrene (Dowex 20 M) and various salts of crosslinked co-poly[styrene-4-vinylpyridine] with hydrogen halides were used as solid catalysts in investigations of the conversion of acids to esters. The role of the structure of the acid (acetic acid, benzoic acid), solvent (n-octane, toluene, n-butanol) and reaction temperature in the presence of polymer supported catalyst was tested in the reaction with n-butanol. Sulphonated crosslinked polystyrene (3a) was the most active catalyst, similar activity was found with crosslinked co-poly[styrene-4-vinyl(pyridinium chloride)], while catalysts bearing a fluoride (3b) and

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*Dedicated to the late Prof. M. Perpar

iodide (3e) function were almost unreactive. The important role of co-solvents was also established.

Chemical transformations of polymers offer an attractive possibility for the preparation of new catalysts, reagents, separation media, etc. and found increasing popularity in the last twenty years [1 - 6]. It is known that the reactivity of such a catalyst strongly depends on the structure of the polymer backbone (polarity, crosslinking, etc.). The structure and the amount of the active group introduced into the polymer backbone, the solvent (polarity - swelling of the polymer resin, viscosity, steric interactions, acidity or basicity and ability to form hydrogen bonds with the catalyst) and the structure of the organic molecules are usually more important than in the case of the corresponding homogeneous reactions. The role of the above mentioned variables have been discussed recently [7].

The synthesis of esters is one of the most important processes in organic chemistry [8] and is also of great industrial importance, being usually curried out today in the presence of a solid catalyst in the vapour or liquid phase. The choice of the type of catalyst depends on the synthetic strategy. Preparation of esters from acid chlorides or acid anhydrides usually requires a catalyst bearing basic units. In recent years, extensive studies were made of polymer-bound dimethylaminopyridine [9 - 16], while Frechet and coworkers [17] examined the effect of local reaction medium and catalyst efficiency. Recently, we have also pointed out the importance of the polymer structure when containing units of basic character (pyridine, butylamine, piperidine, piperazine etc.) in the reactions of acid chlorides and anhydrides with alcohols [18].

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On the other hand, direct conversion of acids to esters with alcohols usually requires the presence of an acid catalyst. In Scheme 1 three possible pathways (A, B and C), which must be taken into account when insoluble organic catalysts are used for acid catalysed esterification, are present. Solvent penetrates into insoluble resin and can swell it (species I), or can form a solvent-separated ion-pair (species II) (equilibrium process). Acid can penetrate into swollen resin (1) and associate with an ionized acid group forming species (IV), which further reacts with alcohol to form an ester; the process following pathway A usually behaves as a heterogeneous catalysed reaction. Penetration of alcohol into the swollen resin (I), pathway B, results in the formation of the solvent-separated ion-pair (III) (equilibrium process). Pathways B or C, involving species II or III, usually represent pseudo - homogeneous reactions catalysed by solvated protons. Which pathway (A, B or C) predominates in the acid catalysed conversions of acids to esters depends on the structure of the catalyst, the solvent, the structure of the acid and the alcohol, and the type of operation (continuous or batch process), and usually competition between these various processes is observed.

The use of insoluble catalysts offers the following advantages over homogeneous catalysts:

1. the catalysts are easily separated from the reaction mixture
2. a higher degree of selectivity can be achieved in comparison to homogeneous catalysis
3. undesirable side reactions can often be avoided

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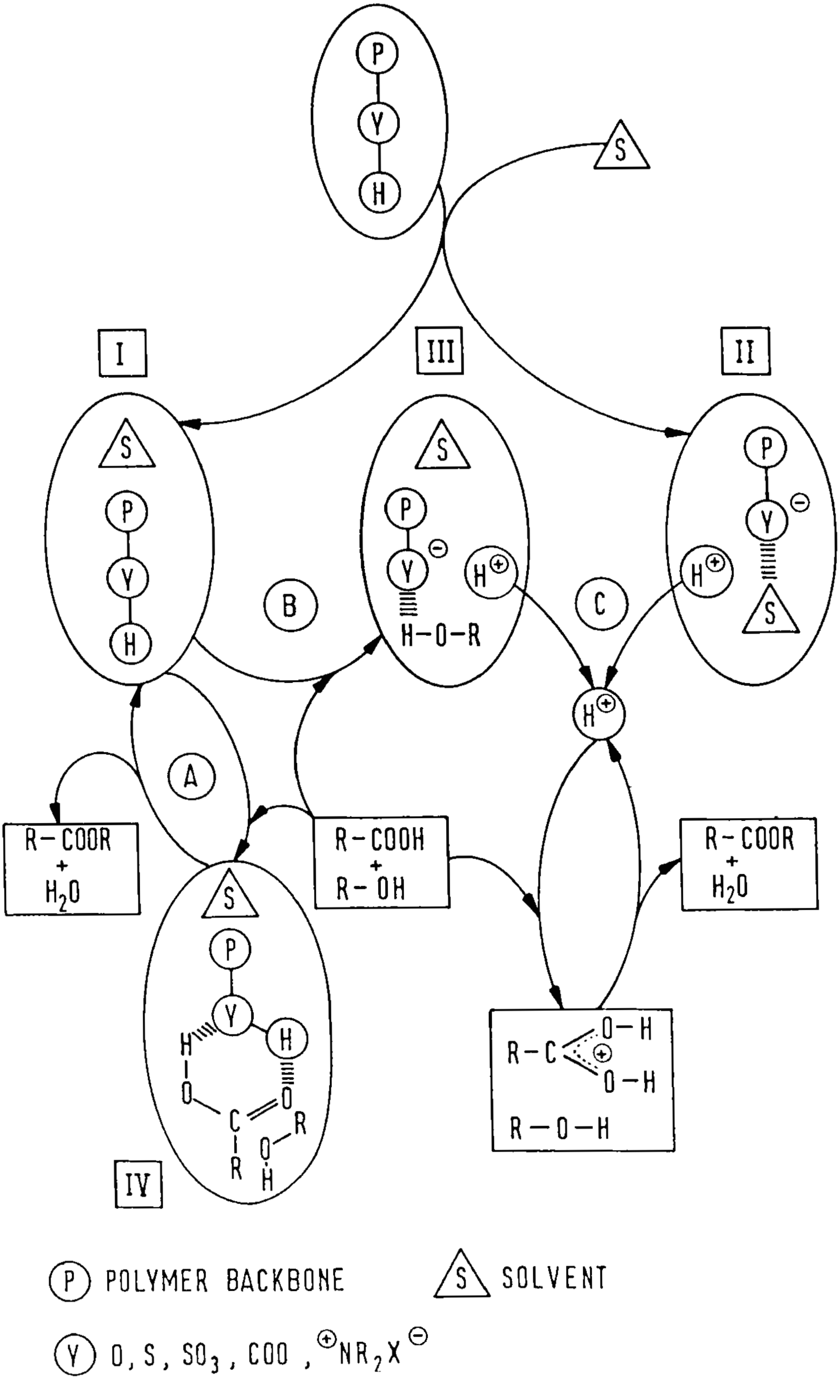
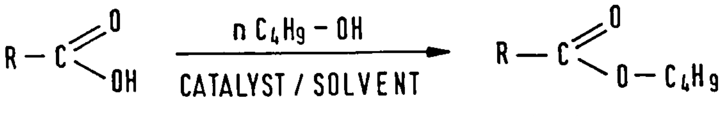


SCHEME 1

4. a solid catalyst permits operation in either continuous or batch process
5. corrosion processes are reduced or even eliminated.

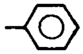
The esterifications of acids with alcohols in the presence of crosslinked polystyrenesulphonic acid were studied extensively and it was considered that alcohol and water solvated the sulpho groups. The esterification of octanoic acid with n-butanol consists of a heterogeneous reaction catalysed by unionized sulpho groups and a pseudo - homogeneous reaction, catalysed by solvated protons [19]. Correlations with the results of reactions in which protic solvents were excluded suggest that the position of the equilibrium of the solvent-separated ion-pair formation depends mainly on the electron - donor properties of the solvent [20]. Solvents with a strong donor property diminish the number of unionized sulpho groups, which act as catalysts species for heterogeneous reactions. The important role of the solvent and polarity inside or outside the resin was also demonstrated by conversion of benzoic acid with n-butanol to ester in the presence of an insoluble catalyst [21].

The important role of polymer bonded catalyst structure on the conversion of organic molecules stimulated us to study the effect of polymer catalyst on the conversion of acetic and benzoic acid to esters with n-butanol (Scheme 2). The question of the swelling of the resin versus solvent polarity arises in these transformations, and for this reason we measured the swelling capacity of the catalysts in various solvents. As is evident from Scheme 2, in the nonpolar solvent n-octane all resins remained almost unchanged, while swelling was also suprisingly small in

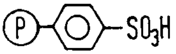
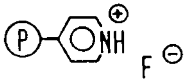
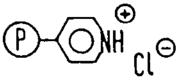
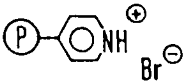
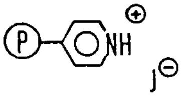


(1) (2)

(1a) : R = – CH_3

(1b) : R = 

THE EFFECT OF CATALYST STRUCTURE ON DEGREE OF SWELLING IN VARIOUS SOLVENTS

CATALYST	SOLVENT			
	n C_8H_{18}	$C_6H_5CH_3$	n C_4H_9OH	$HCON(CH_3)_2$
 (3a)	1.0	1.0	1.3	1.4
 (3b)	1.0	1.0	1.0	2.3
 (3c)	1.1	1.1	1.7	2.3
 (3d)	1.0	1.0	1.4	2.5
 (3e)	1.0	1.2	1.1	3.3

SCHEME 2

toluene (uncharged crosslinked polystyrene and crosslinked poly[4-vinylpyridine] type resins are swollen very much in aromatic solvents). The stucture of the catalysts influenced swelling in n-butanol, where hydrofluoride (3b) and hydroiodide (3e) resins remained almost unswollen, while a very large degree of swelling was observed for resins bearing pyridine rings in N,N-dimethylformamide.

Crosslinked poly[styrene-4-vinylpyridine] (crosslinking 2%, containing 37% pyridine rings) was converted to the coresponding halide containing resin (3b-3e) by swelling the polymer beads in chloroform, followed by introduction of gaseous hydrogen halide until saturation of the reaction mixture. After work-up, the polymer beads were analysed. In the case of fluoride resin 14.35% fluoride was found which means that each pyridine rings bears two fluoride anions, while functionalization with hydrochloride and hydrobromide, as shown previously [22], leads to a product in which each pyridine ring was functionalized by one hydrohalide molecule. Under the above mentioned procedure lower functionalization was established in the case of resin (3e) (24.8% of iodide).

First we studied the effect of the catalyst, reaction temperature and time on the conversion of acetic acid to n-butyl acetate. As is evident from Table 1, sulphonated resin (3a) and poly[styrene-4-vinylpyridine] hydrochloride (3c) were the most effective, while the solvent polarity influenced the conversion in a different way. Pyridine - bearing catalyst (3c) in n-butanol was the most effective, while in n-octane the reactivity shape changed a little and became reversed in toluene, when comparing

TABLE

THE EFFECT OF THE STRUCTURE OF THE ORGANIC MOLECULE (1), CATALYST (3), AND SOLVENT ON THE FORMATION OF ESTER (2).

n-BUTYL ACETATE[a]					
CATALYST	T[°C]	TIME	SOLVENT		
			n-C_8H_{18}	$C_6H_5CH_3$	n-C_4H_9OH
(3a)	80	2	100%	100%	100%
	50	1	56%	64%	88%
(3b)	80	2	5%	2%	10%
(3c)	80	2	100%	98%	100%
	50	1	49%	28%	91%
(3d)	80	2	87%	71%	90%
(3e)	80	2	3%	1%	11%
NONE	80	2	1%	1%	5%
n-BUTYL BENZOATE[b]					
(3a)	100	5	94%	61%	92%
	80	2	9%	7%	13%
	50	1	1%	2%	2%
(3c)	100	5	7%	1%	45%
	80	2	2%	1%	10%
(3d)	100	5	3%	1%	30%

a.) 5 mmol of acetic acid, 10 mmol of n-butanol, 250 mg of catalyst 3 and 5 ml of solvent (in the case of n-butanol no solvent was used),

b.) 3 mmol of benzoic acid, 6 mmol of n-butanol, 150 mg of catalyst 3 and 3 ml of solvent data with sulphonated polystyrene (3a). Changing the halogen from chloride to bromide diminshed the conversion of acid to ester in all solvents studied, while suprisingly the resins bearing fluoride and iodide (3b and 3e) appeared to be almost ineffective for this kind of transformation of organic molecules (this ineffectiveness, however, is paralled by the very small degree of swelling in n-octane, toluene and n-butanol).

Usually aromatic solvents swell polymeric catalysts very well, which means that they penetrate efficiently to the polymer matrix. However, as shown in Scheme 2, charged resins remained almost unchanged in toluene and for this reason we extended our studies to an aromatic acid. It can be seen from the Table that conversion of benzoic acid after two hours at 80^{0}C in the presence of sulphonated polystyrene (3a) dropped dramatically. Conversion could of course be enhanced if a longer reaction time and higher temperature were used. However, it is interesting that in the case of the conversion of benzoic acid to ester, the polystyrene type of catalyst (3a) was more effective than chloride resin (3c). A larger effect of solvent on the conversion was also found. Reactions of benzoic acid in n-octane and toluene in the presence of 3c and 3d were very slow.

In order to obtain more information about the course of the reaction (Scheme 1), 200 mg of polymer beads were stirred in 20 ml of a mixture of methanol and water (1 : 1) for one hour, filtered off, washed with 20 ml of water-methanol mixture, and finally titrated with water solution of sodium hydroxide. It was found that the solution after stirring the polystyrene resin (3a) contained only 0.08 mmol of acid per gram of resin, while the amounts were much higher for resins (3b-3d) (0.9 mmol per gram of resin for 3b, 1.1 mmol for 3c, 1.0 mmol for 3d, 0.4 mmol for 3e). A lower acidity of the filtrate was observed when hydrochloride resin (3c) was stirred in n-butanol (0.4 mmol per gram of resin).

Further, we also studied the effect of a loss of catalytic capacity of insoluble resin. 250 mg of polymer catalyst (3c) was suspended in a mixture of 5 ml of n-octane, 5 mmol of acetic acid and 10 mmol of n-butanol and heated for 2 hours at 80^{0}C. Polymer beads were filtered off and the filtrate analysed by GLC. In the first reaction, complete conversion of acid to ester was found, while in the second experiment unregenerated resin was used and a 16% diminished conversion was found, while in the third experiment the conversion dropped to 64, and to 44% in the fourth cycle. However, the resin can be easily regenerated, by suspending the beads in chloroform and addition of hydrohalogen.

The present study again confirms the important role of the structure of the catalyst, the solvent and the structure of the organic molecule in such reactions, and the fact that the results found cannot be predicted in advance. Much more work is needed to understand the role of the above mentioned parameters on the transformations of organic molecules.

EXPERIMENTAL

Gas liquid partition chromatography was carried out on a Varian Aerograph 3700 with a LDC/Milton Roy CI-10-B integrator.

Poly[styrene-4-vinyl pyridine], containing 2% DVB and 37% of pyridine rings (%N = 5,0) was prepared according to the literature [22]. Halide (chloride, bromide and iodide) contents were determined by potentiometric titrations [23] with silver nitrate and a silver electrode using an ISKRA MA 5705 pH meter. Fluoride was determined in the Fluorine Chemistry Department at the "J. Stefan" Institute.Sulphonated polystyrene (Dowex 50 W) was purified in methanol, crushed, and dried at room temperature for 18 hours.Solvents and reagents were purified before use [24].

Preparation of catalysts 3b, 3c, 3d and 3e

15 g of poly(styrene-4-vinylpyridine) were suspended in 200 ml of chloroform, swollen for 18 hours at room temperature and cooled on an ice-salt bath. During one hour 3 mmol of gaseous hydrogen halide per mmol of pyridine ring were supplied to the reaction mixture, which was then warmed to room temperature and stirred for 20 hours. Insoluble resin was filtered off, washed with 500 ml of chloroform and dried in vacuo at 23°C for 18 hours. For elemental analysis the polymer resin was dried for 3 hours at 80°C. Polymer catalyst 3b contained 14.4% of fluoride, 3c 10.0% of chloride, 3d 20.4% of bromide and 3e 24.8% of iodide.

Determination of Degree of Swelling

To 1 ml of dry catalyst 3 in a graduated cylinder, 5 ml of solvent were added and left to swell for 24 hours at room temperature and the final volume of the swollen resin was measured.

$$\text{SWELLING} = \frac{\text{V of swollen resin}}{\text{V of dry resin}}$$

Esterification Procedure

5 mmol of acid and 10 mmol of alcohol were dissolved in 5 ml of solvent (in the case of the preparation n-butylacetate in n-butanol no solvent was used). 250 mg of polymer catalyst 3 were suspended in the

reaction mixture and stirred at a given temperature for a given time. Insoluble resin was filtered off and washed with 5 ml of chloroform.
The reaction mixture was analysed by glc (n-butylacetate: FFAP 5%, Chromosorb W AW 80/100, temperature program 60 - 130°C; n-butylbenzoate: OV - 17 10%, Chromosorb W AW 80/100, temperature program 60 - 190°C, internal standard: camphor).

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