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STUDY OF ALKYLATING REACTIONS CATALYSED BY CATION-EXCHANGE RESINS

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SUMMARY

The possibilities of industrial uses of various cation-exchange resins have been studied in acetic acid esterification reactions. Catalytic activities and life-times of resins have been studied and compared. The oleophilic sulphonated styrene-vinylbenzene polymer has been proven to be the best, its activity being similar to that of sulphuric acid and can be used in 50 esterification cycles without regeneration. It has been observed that stirring increases the rate of esterification reaction, but decreases the lifetime of the resin. The reactions studied have been catalysed by the ion-exchange resin, independently of the structure of alcoholic components. It is advantageous to perform esterification at the boiling point of the mixture in order to evaporate the water produced. To avoid boiling temperatures exceeding 160°C, the addition of certain solvents might be necessary. Applying strong cation-exchange resins, alcohols can be used for aromatic C-alkylation of phenols, but the alkyl group will be isomerised, and an olefin compound beside an aliphatic ether are produced in simultaneous reaction.

INTRODUCTION

Cation-exchange resins are well-known catalysts of intermolecular and intramolecular condensations. The alkylating processes are of great importance in the intermolecular reactions. Several authors have studied O-alkylation^{1–7}. Very few references are to be found in the literature, however, on C-alkylation^{8–12}.

The authors have studied O- and C-alkylating reactions catalysed by various cation-exchange resins. Our aim was to study the parameters technologically significant in esterification reactions, and to investigate the side-reactions to be expected in C-alkylation of aromatic compounds.

EXPERIMENTAL CONDITIONS

Our experiments have been performed in glass reactors equipped with thermom-

eters, goosenecks, and a combined reflux-cooler, at the boiling point of the reaction mixture. Water containing solvent mixture had been evaporated at the mentioned temperature out of the reactor until the water produced in the reaction has been completely removed. The other components of the distillate were recirculated into the reaction mixture after separation. To avoid degradation of cation-exchange resins in reaction mixtures with high boiling points, the water has been removed by azeotropic distillation with cyclohexane. In the various stages of our study, a total of 8 cation-exchange resins have been studied. Their main properties are summarized in Table I.

TABLE I
CHARACTERISTIC DATA OF CATION-EXCHANGE RESINS STUDIED

<i>Resin</i>	<i>Trade name</i>	<i>Matrix</i>	<i>Ionic group</i>	<i>Morphologic character</i>	<i>Capacity (mequiv./g)</i>
E	Wofatit F	phenolic resin	-SO ₃ H	porous	2.9
F	Wofatit P			porous	1.9
G	Lewatit SP 120	polystyrene resin	-SO ₃ H	porous	4.8
A	Varion KS			gel	4.9
C	Varion KSB			gel	4.9
B	Varion KSM			porous	4.9
H	MÜKI OLS			oleophilic polystyrene	gel
D	Varion KCO	polystyrene resin	-COOH	gel	

In the O-alkylating reaction, 1 mol of acetic acid, 2 mol of alcohol and 10 g of ion-exchange resin, (air-dry, in the H⁺-form) have been mixed. In the C-alkylating reactions, 0.3 mol of alcohol, 0.3 mol of aromatic compound and 4.5 g of cation-exchange resin, similar to the ones mentioned above, have been used.

In O-alkylations, the reactions have been monitored by acidimetric titration, whereas in C-alkylations the quantity of water produced has been measured.

The products in liquid state have been fractionated after the end of the reaction. The fractions, compared with test samples, have been identified by gas chromatography and infrared spectrophotometry. Products in gaseous state have been collected in gas-burettes. Their analyses have been performed by gas chromatography.

EXPERIMENTS

Catalytic activity (Fig. 1), lifetime (Table II) of the resins as well as the effect of stirring on the reaction (Fig. 2) and on the lifetime of the resin (Fig. 3) were studied in O-alkylating reactions. The effects of the presence of water (Table III) in the system was separately investigated.

Following this, the possibilities of producing acetic esters of C₃-C₈ aliphatic alcohols have been investigated by the Varion KSM resin (Table IV) (Figs. 4 and 5, respectively).

The alkylation of aromatic compounds, toluene (I), anisole (II), phenol (III) and *p*-cresol (IV), was carried out by means of *n*-butyl and *sec*-butyl alcohols in the presence of an ion-exchange resin (Lewatit SP 120). The purpose of the experiments

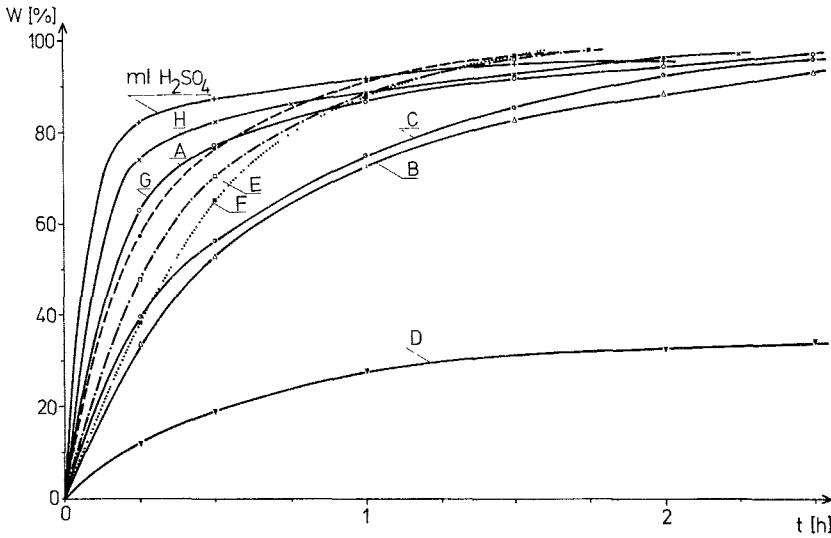


Fig. 1. Production of butyl acetate with various catalysts. See Table I for names of resins.

TABLE II

LIFETIMES OF VARIOUS CATION-EXCHANGE RESINS IN BUTYL ACETATE ESTERIFICATION REACTIONS

Acetic acid-butyl alcohol (1:2); 10 g resin per mol acetic acid.

Type of resin	Useful lifetime		Catalytic effectivity (mol acetic acid/g resin)
	cycles	h	
Varion KS	57	110.0	5.7
Varion KSM	9	22.5	0.9
Wofatit P	12	25.0	1.2
Wofatit F	26	53.3	2.6
MÜKI OLS	48	60.0	4.8
Lewatit SP 120	62	108.0	6.2

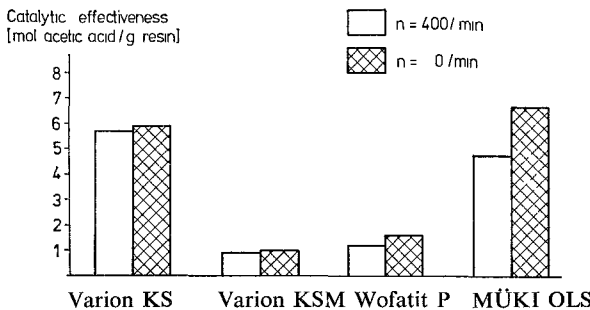


Fig. 2. Effect of stirring in butyl acetate esterification catalysed by Varion KSM.

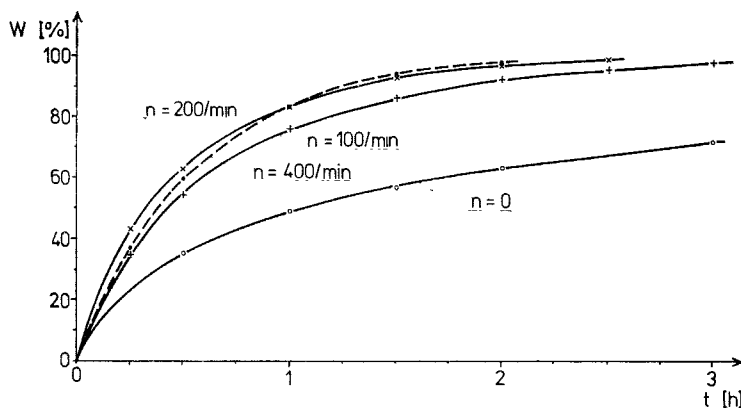


Fig. 3. Effect of stirring on the lifetime of resin in the production of butyl acetate.

TABLE III

PRODUCTION OF BUTYL ACETATE IN CYCLOHEXANE SOLUTION

Acetic acid and butyl alcohol, 1 mol/dm³; Lewatit SP 120, 20 g.

W = conversion, k = reaction rate constant, n = apparent order of reaction.

	T (°C)	$W = 0-35\%$		$W = 35-60\%$	
		k (M^{1-n}/min)	n	k (M^{1-n}/min)	n
Without distillation	76-77	0.017	2.2	0.009	0.7
With distillation	80-81	0.022	1.4	0.022	1.4

TABLE IV

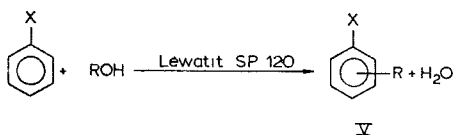
TEMPERATURES OF THE ESTERIFICATION REACTIONS STUDIED

Acid component, acetic acid.

Reaction No.	Alcohol component	Temperature of reaction (°C)	
		Without solvent	In cyclohexane solvent
1	Butyl alcohol	110-118	
2	Pentyl alcohol	110-135	100-125
3	Heptyl alcohol	135-170	110-155
4	Octyl alcohol	160-195	145-170
5	2-Methyl-1-propanol	110-118	
6	2-Ethyl-1-hexanol	150-184	
7	Propyl alcohol	—	90-96
8	Isopropyl alcohol	—	82-87

was to study all the intermolecular and intramolecular dehydration reactions of the alkylating alcohols.

The alkylating reaction has been performed according to eqn. 1.



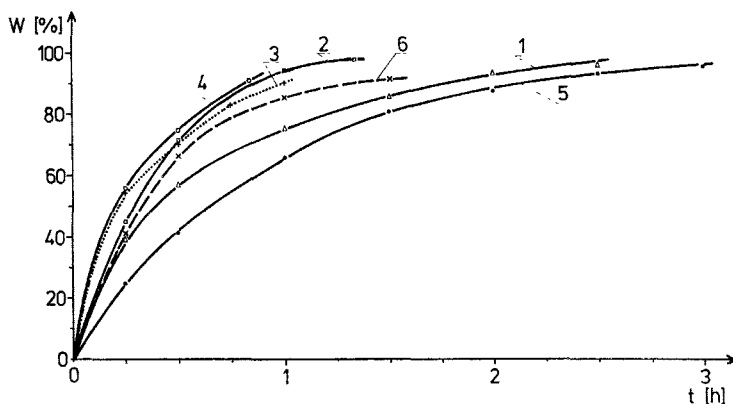


Fig. 4. Esterification of acetic acid with various aliphatic alcohols. See Table IV for number of the reaction.

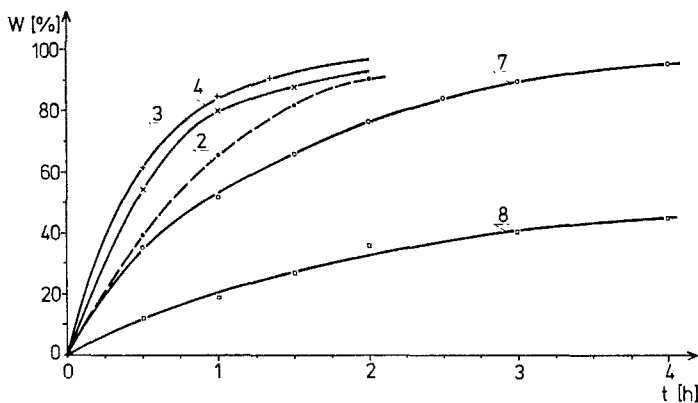
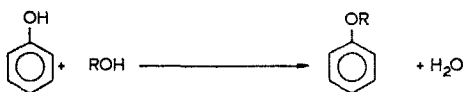
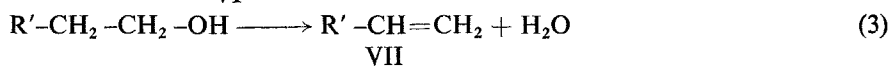
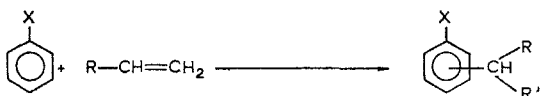


Fig. 5. Esterification of acetic acid with various aliphatic alcohols in cyclohexane solvent. See Table IV for number of the reaction.

In addition to the suspected reaction, the following side-reactions should be taken into consideration:







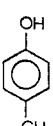
VIII



IX

The results are summarized in Table V.

TABLE V
FRIEDEL-CRAFTS REACTION STUDIED

Substrate	Active component	Temperature (°C)	Time (h)	H ₂ O (mol)		Products		
				ROH (mol)	Reaction No.	Yield (%)	Isomers (%)	
	CH ₃ -(CH ₂) ₃ -OH	98-100	36	0.96	VII VI V	15 30 1	<i>m, p</i>	
	CH ₃ -CH-C ₂ H ₅ OH	110-128	7	0.73	VII VI IX	85 5 1		
	CH ₃ -(CH ₂) ₃ -OH	110-138	55	0.85	VII VI IX	30 33 11	<i>m:9</i> <i>p:2</i>	
	CH ₃ -(CH ₂) ₃ -OH	123-143	35	0.89	VII VI VIII IX	20 41 0.5 34.5	<i>m:14.5</i> <i>p:20</i>	
	CH ₃ -(CH ₂) ₃ -OH	124-148	38	0.95	VII VI IX	20 50 32.5		

RESULTS

O-Alkylations have been catalysed by resins having only -SO₃H groups. Their activities are lower than that of sulphuric acid catalysts used in such reactions. The ion-exchange capacities and morphologic properties of ion-exchange resins have no direct correlation with their catalytic activities (Table I, Fig. 1). Similarly, no relationship could be demonstrated between the above properties and the lifetimes of the catalytic activity (Table II). Stirring, not depending upon its intensity, increases the rate of reaction, but it decreases more or less the lifetime of the catalytically active resins (Fig. 3). The last effect depends upon the stability of the carrier. The rate of reaction was decreased by the presence of water (Table III).

CONCLUSIONS

Based upon C-alkylation experiments (Table V), it can be stated that under selected conditions, alcoholic alkylation will take place only on aromatic rings containing free phenolic hydroxyls (III, IV). In all other cases only products of intramolecular and intermolecular dehydration could be demonstrated. The proportion

of the two products possibly depends on the sorptions of the reactants by the resin. By alkylating phenol this way, corroborates with the theory that cation-exchange resins do not form complexes with hetero-atoms, since this would deactivate the aromatic compound.

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