

## THE EFFECT OF THE CROSSLINKING OF ION EXCHANGERS ON THEIR CATALYTIC ACTIVITY FOR REESTERIFICATION

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Reaction rates of five different reesterifications of aliphatic esters by alcohols in the gas and liquid phase have been measured using standard and macroporous sulphonated styrene-divinylbenzene copolymers with different degree of crosslinking as catalysts. The effect of crosslinking of the catalysts on reaction rate is discussed. The principal difference has been found between gas phase and liquid phase reactions. A detailed kinetic analysis of the above reactions has shown that the change in the crosslinking of the catalysts reflects in the values of the rate constants of the kinetic equations of studied reactions, but the values of their adsorption coefficients remain the same within the accuracy achieved. The attempt has been made to estimate the effect of crosslinking of the catalysts on the selectivity of parallel reesterifications.

The degree of the crosslinking of macromolecules of organic ion exchangers affects their catalytic activity in gas phase as well as liquid phase reactions. This follows from some of our previous works<sup>1,2</sup> and also from studies by other authors<sup>3-17</sup>. With unporous, standard ion exchangers the reaction rate decreases with increasing degree of crosslinking on account of the lesser accessibility of functional groups. In the case of macroporous ion exchangers the course of the dependence of the reaction rate on the degree of crosslinking depends upon whether the reaction is performed in gas or liquid phase. The reaction rate of gas phase reactions increases with increasing crosslinking on account of increasing surface of ion exchangers, while for liquid phase reactions the dependence of the reaction rate acquire different forms, according to how strong is the effect of geometrical surface and of swelling of ion exchanger mass. Also studied was the effect of the structure of reactants on the rate of reactions catalysed by ion exchangers<sup>18-20</sup>. It was shown that the reaction rate decreases with increasing size of reacting molecules. In addition, especially in the liquid phase, the character of reacting substances affects also physical influencing of the ion exchanger (*e.g.* its swelling), which reflects in changes in the reaction rate.

In most of the studies mentioned the authors have dealt with the effect of the degree of crosslinking on the rate of reactions catalysed by ion exchangers only superficially. For that reason the present work is devoted solely to this problem with the aim to get information about as broad range of considered parameters as possible. We have measured reaction rates of reesterification of aliphatic esters with aliphatic alcohols. These reactions were used by us already earlier<sup>18,21</sup> and thus basic data about their rate have been available. By comparison of reaction rates

of different reactions for the same set of catalysts we attempted to characterize the effect of crosslinking on the selectivity of the catalytic effect of ion exchangers.

### EXPERIMENTAL

*Compounds used.* Methanol, 1-propanol, 2,2-dimethylpropanol, ethyl acetate, and ethyl formate were commercial products (Lachema, Brno) of technical purity grade. They were dried over magnesium sulphate and purified by rectification prior to using. Ethyl isobutyrate was prepared by the liquid phase esterification of isobutyric acid with ethanol catalysed by sulphuric acid, dried after isolation and rectified similarly as the other substances. All the compounds used contained less than 0.3% of water (by K. Fischer method) and their boiling points agreed with reported data. They did not contain further admixtures, as proved by gas chromatography.

*Catalysts.* Catalysts employed were sulphonated styrene-divinylbenzene copolymers of standard and macroporous type. These were the same as in some of our previous works<sup>1,2</sup>. Some of their properties are summarized in Table I. The particle size of the ion exchangers was 0.16 to 0.3 mm. The ion exchangers were dried *in vacuo* (14 Torr) for 6 h at 105°C before use. They were stored in a desiccator over phosphorus pentoxide.

*Apparatus and procedure.* Gas phase reactions were carried out in a glass flow reactor at 120°C. A mixture of liquid reactants was fed by the known constant rate to an evaporator, along with a stream of inert carrier gas (nitrogen). The reaction mixture passed through the catalyst bed (0.05–1 g). Liquid reaction products were separated from nitrogen by condensation at –78°C. Experiments were carried out to conversions not exceeding 10%, which rendered it possible to determine the values of initial reaction rates directly from conversions and contact times

TABLE I  
Some Properties of Ion Exchangers Used

Denotation <sup>a</sup>	Exchange capacity meq/g	Specific surface m <sup>2</sup> /g	Porosity <sup>b</sup> %
SS-2	4.90	<0.1	—
SS-8	4.75	<0.1	—
SS-15	4.38	<0.1	—
SS-25	3.72	<0.1	—
SS-50	1.97	<0.1	—
MS-10	4.00	16	13
MS-15	3.81	35	45
MS-25	3.80	44	58
MS-40	3.20	120	59
MS-60	3.02	227	63

<sup>a</sup> SS standard sulphonated copolymers, MS macroporous sulphonated copolymers, the number refers to the content of divinylbenzene (in %) in the polymerization batch. <sup>b</sup> Porosity was calculated from the values of mercury and helium density of ion exchangers.

of the reactants. Liquid phase reactions were performed in a glass ideally mixed (about  $100\text{min}^{-1}$ ) flow reactor at a temperature of  $52^\circ\text{C}$  (in some cases at  $70^\circ\text{C}$ ). The correct performance of the reactor was verified according to Bennett<sup>22</sup>. The samples for analysis were withdrawn in the time when the reactor worked under steady state conditions. Because of the differential character of the reactor, the values of the reaction rates were obtained directly from the values of the conversions and flow rates of reactants.

*Analysis.* The products of the reactions of ethyl acetate and ethyl isobutyrate with propanol were analysed chromatographically at  $88^\circ\text{C}$  with the use of dinonyl sebacate (15%) on Celite which was placed in a  $340\text{ cm} \times 4\text{ mm}$  column. The products of the other reactions were analysed similarly at  $80^\circ\text{C}$ , using poly(ethylene glycol) 400 (15%) on Celite and the same column. In both cases the carrier gas was nitrogen and the detector was a flame-ionization one.

## RESULTS AND DISCUSSION

In Table II are given the values of initial rates ( $\text{mol/h kg}_{\text{cat}}$ ) of all the esterification reactions measured on the ion exchangers presented in Table I, and that both in the gas phase and in the liquid phase. Because of low rates of liquid phase reesterifications, some systems were measured at a temperature of  $70^\circ\text{C}$ . In all cases, however, we have followed the condition that each reaction on a given series of the catalysts (MS-10 to MS-60 or SS-2 to SS-50) was measured under identical conditions, *i.e.* the same temperature, the partial pressure of reactants and the contact time of the reaction mixture.

From the values of the initial rates shown in Table II some conclusions can be made concerning the effect of the degree of crosslinking of the ion exchangers upon their catalytic activity. For the macroporous ion exchangers and gas phase reactions the reaction rate increases with increasing crosslinking. Since in gas phase reactions it seems unlikely to expect that the reaction components penetrate more significantly to the ion exchanger mass, the reaction rate is determined above all by the magnitude of the geometrical surface of the catalyst. Relatively small differences in the reaction rate between MS-40 and MS-60 can be accounted for by the fact that in these ion exchangers a considerable part of the surface resides in the pores of 2–3 nm diameter, to which an access of the molecules of the reactants is difficult and hence this surface is not catalytically exploited (see the diagram of the pore distribution for these ion exchangers presented in the previous work<sup>2</sup>). In the case of the gas phase reactions on standard ion exchangers, the reaction rate decreases with increasing crosslinking. Here, the surface of the catalysts play essentially no role and the rate of the catalytic reaction is given only by the number of accessible functional groups within the mass of the polymer substance. As to the least crosslinked ion exchanger SS-2, a relatively great number of molecules of reactants penetrate into the mass, by which they can interact with catalytically active functional groups and the reaction rate is comparatively high. As the degree of crosslinking increases the permeability of the ion exchanger particles diminishes and the reaction rate slows down.

In the case of the liquid phase reactions catalysed by standard ion exchangers the reaction rate decreases with increasing crosslinking of ion exchangers, similarly as in the gas phase. Also reasons are analogous. In addition, the reaction rate is also affected by swelling of ion exchangers in the solvent. The ion exchangers with low degree of crosslinking swell much more, by which the accessibility for reactants of their functional groups within particles increases. That is why also the ratio of the reaction rates for SS-2 and SS-50 is much greater for liquid phase reactions compared to that for the gas phase reactions (see the coefficient  $P$  in Table II).

In the case of the macroporous ion exchangers the rate of the liquid phase reactions depends upon the degree of crosslinking only very little. In some cases it is even independent. This is likely due to the mutual effect of varying surface of the ion exchangers and of swelling of their polymer mass in the reaction system. The ion exchangers with lower degree of crosslinking have a relatively small geometrical surface but they swell considerably, in the highly crosslinked ion exchangers, however, only a part of the overall geometrical surface participates in the reaction since the pores of smaller dimensions are closed by the swelling of the polymer mass. Both effects act against each other and, hence, they eliminate its influence on the reaction rate. Reaction rates have been measured in the liquid phase reactions on macroporous ion exchangers also in cyclohexane as the solvent. As found earlier<sup>23</sup>, the reesterification in cyclohexane catalysed by ion exchangers has a different kinetics. Furthermore, the polymer mass of the ion exchangers swells to a lesser extent in cyclohexane than it does in dioxane. From Table II it follows, however, that the dependence of the reaction rate upon the degree of crosslinking is similar for both solvents, small differences being observed only in the absolute values of the initial rates.

In our previous work<sup>1</sup> we have found for the sorption of organic compounds on ion exchangers that the absorbed amount depends upon the size of organic molecules as well as on their chemical character. As in this work the values of reaction rates are discussed in relation to the accessibility of functional groups of a catalyst for reactants, the above mentioned factors should also play a role in our case. The chemical character of the reactants changes only very little and therefore its more important effect seems improbable.

The more substantial differences exist in the size of the reactants. From the coefficient  $P$  in Table II, which express the quotients of the rates on ion exchangers with the maximum difference in crosslinking, it is seen that these are greatest for the reactions of 2,2-dimethylpropanol with ethyl isobutyrate. As these substances have bulkiest molecules, the difference in their reactivity can be ascribed to the greatest decrease in the extent of penetration into the mass between low- and high-crosslinked catalysts. The effect discussed is more pronounced in gas phase reactions, since ion exchangers in dry state exert the more distinct sieve effect than in the swelled state in liquid medium.

TABLE II  
Initial Reesterification Rates (mol/h kg<sub>cat</sub>) on Standard and Macroporous Ion Exchangers in Gas Phase and Liquid Phase

Reaction <sup>a</sup>	MS-10	MS-15	MS-25	MS-40	MS-60	<i>P</i> <sup>b</sup>
Gas phase						
(A)	5.94	9.81	13.54	17.54	16.30	2.74
(B)	0.34	1.29	2.60	2.77	3.00	8.82
(C)	0.82	3.74	7.00	7.22	7.44	9.07
(D)	15.93	36.61	55.93	70.51	76.27	4.79
(E)	378.2	692.3	807.7	846.2	859.0	2.27
Liquid phase (dioxane)						
(A)	4.44	3.85	3.60	4.51	4.38	1.01
(B) <sup>c</sup>	1.22	0.91	0.88	0.84	0.93	1.31
(C) <sup>c</sup>	1.94	2.05	1.86	1.88	1.90	1.02
(D)	54.3	38.4	32.5	22.5	24.5	2.22
(E)	790.3	621.0	516.1	395.2	362.9	2.18
Liquid phase (cyclohexane)						
(A)	5.95	3.40	3.23	3.48	3.97	1.49
(B)	0.27	0.20	0.22	0.26	0.27	1.00
(C) <sup>c</sup>	6.50	5.82	6.21	6.33	6.41	1.01
(D)	41.22	34.54	29.30	23.92	23.02	1.79
(E)	1 090.5	742.6	657.0	507.1	481.0	2.27
Gas phase						
(A)	7.50	2.90	1.10	0.50	0.90	8.33
(B)	4.60	1.92	2.40	1.70	0.50	9.20
(C)	3.20	1.95	0.20	0.12	0.20	16.00
(D)	5.25	4.40	2.86	3.36	3.33	1.58
(E)	107.7	96.3	53.6	18.2	11.6	9.28
Liquid phase (dioxane)						
(A)	12.45	5.95	2.03	0.80	0.20	62.25
(B)	2.41	1.20	0.56	0.25	—	24.10
(C) <sup>c</sup>	8.21	4.33	1.65	0.46	0.10	82.10
(D)	104.59	55.78	26.06	13.03	6.32	16.55
(E)	2 099.5	1 047.8	321.4	58.8	26.6	78.93

<sup>a</sup> (A) Ethyl acetate-propanol; (B) ethyl isobutyrate-propanol; (C) ethyl acetate-2,2-dimethylpropanol; (D) ethyl acetate-methanol; (E) ethyl formate-propanol. <sup>b</sup> *P* the ratio of the initial reesterification rates on ion exchangers with the greatest difference in the degree of crosslinking.

<sup>c</sup> Reactions were measured at 70°C.

The experimental data obtained confirm differences in the influencing of reaction rate caused by the crosslinking of ion exchangers. If the effect of crosslinking of ion exchangers upon reaction rate is significantly different for a single reaction, it could be utilized in controlling the selectivity of parallel reesterifications. However, experimental initial rates have been obtained for each reaction studied using different concentrations of the reactants and they can be thus compared providing that the degree of crosslinking influences only the rate constant of kinetic equations, the other constants being unchanged. We have therefore made a detailed kinetic analysis of reesterifications of ethyl acetate and ethyl formate with n-propanol both in the liquid phase and in the gas phase at temperatures which we used to measure the initial rates of the reactions listed in Table II. The results obtained for the gas phase reesterification were calculated from kinetic equation (1) which was taken from our previous work<sup>21</sup>. The results obtained for the liquid phase reactions were calculated from Eq. (2) which was taken from the thesis of Rodriguez<sup>25</sup>.

$$r^0 = kK_A K_B p_A p_B / [1 + K_A p_A + 2(K_B p_B)^{1/2}]^3 \quad (1)$$

$$r^0 = kK_B c_A c_B / (1 + K_B c_B + K_S c_S) \quad (2)$$

It has been established (Table III) that in the kinetic equations it is only the rate constant  $k$  which varies in magnitude and the other constants, which are considered to be the equilibrium constants of the adsorption of the components of the reaction mixture ( $K_A$ ,  $K_B$ , and  $K_S$ ), are constant within the accuracy of the statistical treatment of experimental data. This fact indicates that the change in crosslinking does not influence the adsorption of the reactants A and B and of the inert components of the medium S. This accords with the results reported by Jeřábek<sup>24</sup> who found the independence of the values of the adsorption coefficients of kinetic equations for the gas phase dehydration of tert-butanol on the ion exchangers with decreasing concentration of acid functional groups and is also in harmony with our results<sup>21</sup> which proved that the values of these constants for the reaction component are essentially identical in its reaction with different partners.

If the values of adsorption coefficients do not depend upon the degree of crosslinking of ion exchangers, then from the values of the initial rates given in Table II one can determine the ratio of the rates of two different reesterifications on individual ion exchangers, *i.e.* ascertain how crosslinking of ion exchangers influences selectivity. To eliminate the difference in the reaction rates between single reesterifications (A)–(E) (Table II), the values of the reaction rates for each series of catalysts have been related to the respective lowest reaction rate. By using the so obtained relative reactivities (of which only the maximum value of  $P$  is shown in Table II) the ratio of the relative reaction rates for all possible pairs of the studied reesterification

reactions in liquid phase and in gas phase have been calculated for each type of ion exchangers used. For reesterification on macroporous ion exchangers in liquid phase we have obtained the ratios of the reaction rates close to one. This means that here the effect of crosslinking of ion exchangers upon the selectivity of parallel reesterifications is immaterial. The more important effect of the crosslinking of ion exchangers upon selectivity occurs in the liquid phase reactions on standard ion exchangers. A similar situation arises also in gas phase reesterifications where the effect of crosslinking is again more pronounced for the reactions on standard ion exchangers, compared to the macroporous copolymers.

TABLE III

Values of the Constants of Kinetic Equations for Reesterifications on Ion Exchangers with Varying Degree of Crosslinking

Meaning of symbols:  $k$  rate constant (mol/h kg<sub>cat</sub>);  $K_A$  the adsorption coefficient of ester (l/mol) resp. (atm<sup>-1</sup>);  $K_B$  the adsorption coefficient of alcohol (l/mol) resp. (atm<sup>-1</sup>);  $K_S$  the adsorption coefficient of solvent (dioxane) (l/mol).

Ion exchanger	MS-10	MS-15	MS-25	MS-40	MS-60
Reesterification of ethyl acetate with propanol					
<i>Liquid phase (dioxane)</i>					
$k$	24.8	20.2	22.0	24.2	28.9
$K_B$	5.8	4.8	5.2	1.9	5.2
$K_S$	10.0	10.0	7.7	15.2	12.8
<i>Gas phase (N<sub>2</sub>)</i>					
$k$	169	249	284	1 351	1 000
$K_A$	1.28	0.99	1.00	0.54	0.67
$K_B$	2.4	1.9	2.8	2.1	3.3
Reesterification of ethyl formate with propanol					
<i>Liquid phase (dioxane)</i>					
$k$	861	1 000	—	367	376
$K_B$	0.61	0.46	—	0.70	0.64
$K_S$	5.45	5.07	—	10.0	6.4
<i>Gas phase (N<sub>2</sub>)</i>					
$k$	1 · 10 <sup>4</sup>	3.5 · 10 <sup>4</sup>	3.7 · 10 <sup>4</sup>	1 · 10 <sup>5</sup>	9.6 · 10 <sup>4</sup>
$K_A$	0.19	0.20	0.40	0.19	0.25
$K_B$	1.5	0.65	1.8	0.51	0.82

In general, it can be stated that the stronger effect of crosslinking is observed for those pairs of reesterifications where the more substantial differences take place in the size of molecules of the reactants, such as *e.g.* between 2,2-dimethylpropanol and methanol or ethyl formate and ethyl isobutyrate. This comports with conclusions about the size of reacting molecules discussed earlier in connection with interpretation of the experimental data presented in Table II. The greater ratios of the reaction rates belong always to the lower-crosslinked types of ion exchangers, with the exception of gas phase reesterifications on macroporous samples in which case the observed trend is opposite.

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## ERRATA

### RE-INTERPRETATION OF THE VIBRATIONAL SPECTRA OF ZEISE'S SALT. I. THE NATURE OF THE P-ETHENE BOND

R. ŘEŘIČHA

This Journal 40, 2577 (1975).

In the previous paper<sup>1</sup> (This Journal 40, 2577 (1975)) the following corrections should be made:

1. Line 19 from top of p. 2588 should be read: "Apparently, at least a four-center MO is formed..."
2. The first sentence of the last paragraph on p. 2589 should be read: "Whilst the first radical cation or the  $\pi^*$  states..."

### THE EFFECT OF THE CROSSLINKING OF ION EXCHANGERS ON THEIR CATALYTIC ACTIVITY FOR REESTERIFICATION

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This Journal 42, 979 (1977).

In the Table II on p. 983 should be between the titles Liquid phase (cyclohexane) and Gas phase this line:

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Reaction <sup>a</sup>	SS-2	SS-8	SS-15	SS-25	SS-50	P <sup>b</sup>
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