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Recent Advances in Ion-exchange Catalysis

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Since the last review article on this topic was published by the writer seven years ago, a great deal of experimental information on the use of ion-exchange resins as organic reaction catalysts has become available, the range of techniques for ion-exchange catalysis has been extended, new types of resin have been examined, and some important theoretical generalisations have been formulated. Reviews by Andreas[2], Sugihara[3], Kaldor[4], and Mulder[5] have dealt with various aspects of the problem: the most extensive of these[3] gives 136 references, mainly up to 1960. The present article discusses some theoretical problems in ion-exchange catalysis, and the use of ion-exchange resins as catalysts in the hydration, dehydration, hydrolysis, esterification, alkylation, polymerisation, isomerisation, and condensation of organic compounds. 254 references.

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I. THEORETICAL PROBLEMS IN ION-EXCHANGE CATALYSIS

Helfferich[6] has defined the effectiveness q[1] of an ion-exchange resin, and has related it to the distribution coefficient λ of the reactants between the catalyst phase and the solution phase. He treats the liquid surrounding the resin particles as an inert medium whose only function is to contain and supply the reactants. This outer solution is in equilibrium with an immobile liquid phase in contact with the resin, which is considered to be the true seat of the reaction. Since the immobile liquid is not separated from the active centres of the resin by an interface, Helfferich[6] treats ion-exchange catalysis as a special case of homogeneous catalysis, whilst recognising that (as in the case of heterogeneous catalysis) rate limitation may be associated with inner diffusion effects.

Combining the concept of resin effectiveness with the hypothesis of a quasi-homogeneous reaction, Helfferich[6] examined the relationship between the former quantity and the distribution coefficient of the reactants between the phases.

Defining the distribution coefficient as the ratio of the molalities of the reactant in the resin phase ($\bar{m}_{AB}$) and in the solution phase (m_{AB}), we have

$$\bar{m}_{AB}/m_{AB} = \lambda. \quad (1)$$

Hence, the reaction rate in the presence of the resin can be written

$$v_r = k_r\bar{m}_{AB} = k_r m_{AB}\lambda, \quad (2)$$

whereas under homogeneous conditions the rate is

$$v_h = k_h m_{AB}. \quad (3)$$

Assuming that both rate constants are proportional to the concentration of catalytically active ions (m_{cat}), which are present in equivalent numbers, we have

$$k_r = k_r' m_{cat} \quad (4)$$

$$k_h = k_h' m_{cat}. \quad (5)$$

Substituting the values of k_r and k_h from (4) and (5) into (2) and (3), we finally arrive at

$$q = (k_r'/k_h')\lambda. \quad (6)$$

Eqn. (6) describes the main specific feature of ion-exchange catalysis, and underlines the possibility of differences in the composition of the reacting system as between the resin phase and the bulk of the solution.

The experimental determination of the distribution coefficient presents some difficulties[7], which were ingeniously overcome by Tartarelli in his work on the application of Eqn. (6) to the hydrolysis of a series of aliphatic carbonate esters[7]. Relatively little work of this type has been published so far, but it has already made a significant contribution to our understanding of the influence upon ion-exchange catalysis of the factors which control the distribution coefficient (nature of the solvent, size of the reactant molecules, structure of the resin network).

The stability of the resin in operation is of the utmost importance to the theory and practice of ion-exchange catalysis. The commonly observed loss of catalytic activity of the resin during a reaction is frequently due to a gradual decrease in the number of catalytically active ions. The detailed mechanism of structural changes of this type within cation- and anion-exchange resins has been studied by the writer and his coworkers. A relationship has been established[8,9] between the thermal stability and the catalytic activity of ion-exchange media towards the polymerisation of tertiary pentenes, and the correctness of this approach has been confirmed in a study[10] of the racemisation kinetics of $d(+)$-α-isobutyldesoxybenzoin.

However, it would be wrong to ascribe all changes in activity to desulphonation, deamination, or degradation effects. In some reactions which take place under particularly mild conditions, such as the hydration of propylene oxide[11] and the decomposition of ethyl diazoacetate[12,13], the activity of sulphonated resins is found to decrease quite rapidly although desulphonation under the experimental conditions seems unlikely. It was found that in these systems the pores of the resin particles are blocked by reaction products, and reactant molecules are therefore unable to reach the active sites. The steric hindrance opposing access to some of the counterions present in the resin has been shown[12] to be high enough to prevent alkalimetric titration[14] of these ions at room temperature. The number of hydrogen ions corresponding to the initial exchange capacity can be set free only by boiling the treated resin with an aqueous solution of sodium sulphate. Gaseous nitrogen (produced by the decomposition of the diazoacetate and responsible for the loss of catalytic activity) is released at the same time.

As a result of this blocking effect, the rate constant for the reaction falls quite quickly to some limiting value, whose level is lower, the greater the degree of cross-linking of the resin catalyst. The changes in catalytic activity can be accompanied by changes in the kinetic order of the reaction[13].

In the present case, the change in catalytic activity is described by the equation

$$H = (H_A - H_R)e^{-\frac{\alpha u}{H_0}} + H_R, \quad (7)$$

where H is the activity at the instant when the extent of reaction is u, H_A and H_R are the initial and the final residual activity respectively, H_0 is the ideal activity of the catalyst in the absence of diffusional limitations, α is the activity decrease coefficient (a measure of the probability of retention of gaseous nitrogen in the resin), and e is the base of natural logarithms. Eqn. (7) can be treated as a general equation for the change in activity of a resin under the influence of blocking by any reaction product.

Frisch[15] has discussed the mechanism of the loss of activity of macroporous resins and some special aspects of the kinetics of catalytic reactions in the presence of these resins. A useful attempt is made in that work to identify the optimum catalyst porosity (corresponding to maximum activity).

Saito[16] has produced a mathematical theory of the reaction rate in ion-exchange catalysis, with allowance for the influence of particle size, the degree of cross-linking, and the distribution coefficient of the reactants.

Thus, some attempts at generalising the results of experiments on ion-exchange catalysis have been made during the period covered by the present review. The ultimate objective of the present stage is the development of a full, quantitative theory of reactions proceeding in the presence of ion-exchange resins.

II. ION-EXCHANGE CATALYSIS IN ORGANIC SYNTHESIS

1. Hydrolytic Reactions

Because hydrolytic reactions are reversible, they are seldom carried out (at least for preparative purposes) as batchwise processes[17,18]. The reactor is usually a three-necked flask fitted with stirrer, reflux condenser, and thermometer, held in a thermostat bath. The catalyst is added to the reaction mixture when the desired temperature has been reached. A nitrogen atmosphere is used when the reactants are sensitive to atmospheric oxygen[17].

The static method is useful for determining the distribution coefficient of the reactants and solvents between the resin and the solution phase. The measurement is made rapidly, without allowing the reactant concentrations in the bulk of the solution and in the resin to change[6]. If the cation exchange resin is used in the sodium rather than in the hydrogen forms[7], the risk of hydrolysis during analysis is eliminated.

The static method has occasionally been used to study the kinetics of hydrolysis[19] by keeping the reaction mixture and the catalyst for a known time in sealed tubes in a temperature-controlled centrifuge, quenching the reaction by cooling, and analysing the mixture.

Dynamic methods require more complicated apparatus, but they have been widely used in preparative work[20-22] as well as in kinetic studies of hydrolysis[7,23-25]. The reactor usually consists of a column, packed with a layer of the resin, and carrying a continuous flow of the reaction mixture. The equilibrium can be strongly displaced towards hydrolysis by distilling off the volatile reaction products[20] or by extraction[21]. In this way the efficiency of the apparatus and the yield of the desired product can be made very high[27], and energy losses can be minimised[21]. Some reactions (e.g. the hydrolysis of pentaerythritol trichlorohydrin monobutyrate[22]) can only be exploited under dynamic conditions. Spes[21] has described a rational continuous process which offers quantitative hydrolysis yields with minimum consumption of energy.

The best hydrodynamic flow conditions are obtained with a column packing of sulphonated polystyrene catalyst rings[22] or of ion-exchange resins mixed with porous polyethylene[21].

The following compounds have been hydrolysed with ion-exchange catalysts†: ethyl acetate[27] (KU-1), methyl acetate[28], methyl lactate[29] (Duolite-C25), allyl acetate[30] (Amberlite-IR 120), ethyl malonate[31] (Dowex-50 W), esters of dicarboxylic acids[32] (KU-2), simple vinyl esters of aliphatic and aromatic alcohols[20] (KU-2 and SG-50), saccharose (Amberlite-IR 120 + Amberlite-IRA 410)[33], starch[34] (sulphonated coal), protein fractions of molecular weight 600–2000[35] (KMT), phenylalanine peptides[17] (Amberlite-IR 113), and ethyl iodide[19] (various anion exchange resins). In the latter case the resin plays the part of a reactant, by taking up acidic products and thus displacing the equilibrium in the desired sense.

The most typical saponification catalysts for esters are cation exchange resins in the hydrogen form, occasionally promoted by Ag ions[30,36] or by Group IVB and VB elements of the Periodic Table[29]. In all reactions so far examined, sulphonated resins have been more effective than carboxylic acid resins. Some reactions (e.g. the hydrolytic cleavage of vinyl phenyl ether) occur only on sulphonated resins.

The efficiency of cation exchange resins towards hydrolytic reactions depends not only on the nature of the active groups but also on the structure of the polymer network. Thus, the hydrolysis of Sarin [isopropylmethylphosphonofluoridate (Ed. of Translation)] is hardly catalysed by a sulphonated phenol–formaldehyde cation exchange resin, but it is quite fast in the presence of the sulphonated styrene–divinylbenzene copolymer[37].

Hydrolytic reactions are usually carried out at relatively low temperatures, where the stability of cation exchange resins is fairly high. Hence there is no reason to doubt the good operating lives of cation-exchange catalysts reported in the literature. According to a group of Soviet workers[22], a granular sulphonated styrene–divinylbenzene copolymer, operated intermittently during 3 years for hydrolysis and esterification reactions, has retained its activity for 500 h without regeneration. Mixed resins, containing 50 wt.% of Amberlite-IR 120 in a matrix of polyethylene, showed no detectable change after 5000 h operation[21]. On the other hand, Dowex-50w X 8 cation exchange resin suffered blocking effects, particularly at elevated temperatures, when used as an inversion catalyst for concentrated saccharose solutions[38].

The kinetic aspects of ion exchange catalysis have been investigated in the fullest detail for the case of hydrolytic reactions.

As in homogeneous acid–base catalysis, the rate of hydrolysis in the presence of resins increases (other things being equal) with the number of catalytically active ions. In some reactions (e.g. the hydrolysis of Sarin in aqueous solutions with a sulphonated resin catalyst)[37] the reaction rate is a linear function of the quantity of catalyst added. The specific rate constant of these reactions, referred to 1 g of resin or to 1 mg-equiv. of sulphonic acid groups, is independent of the amount of catalyst. However, these

† Throughout this paper the grade of resin is shown in brackets.

relationships become more complicated when diffusional limitations are involved. The specific rate constant for the inversion of saccharose in aqueous solution[39] decreases continuously from 4.63×10^{-6} to 3.96×10^{-6} s^{-1} mg-equiv.$^{-1}$ on increasing the amount of KPS-200 resin catalyst from 1.16 to 6.87 g. The specific rate constants for the hydrolysis of the diesters of dicarboxylic acids in water–dioxan solutions remain constant as the proportion of KU-2 resin is increased up to 25%,[40] but they begin to fall off at higher concentrations, which the authors ascribe to diffusion-limited access to some of the H^+ ions in the sulphonic acid groups.

As in the case of homogeneous acid–base catalysis, the rate of hydrolysis in the presence of ion-exchange resins is influenced by the strength of the bond being attacked (i.e. by the chemical nature of the compound). However, and in contrast to homogeneous catalysis, the steric factor (defined as the ratio of the size of the reactant molecules to the distance between the counterions of the nearest active groups in the catalyst) plays an important role in ion-exchange catalysis. This effect accounts for the often reported influence of molecular size on reaction rate. Ordyan and coworkers[41] found that methyl acetate is hydrolysed 5 times faster than butyl acetate, and the latter only 1.2 times faster than methyl valerate. The ratio of the rate constants for the esters of the C_5 acids (valeric, trimethylacetic, and isovaleric) is 3.29 : 1.31 : 1, indicating that the reaction is retarded by branched chains: similar effects have also been observed[7] with n- and isopropyl acetate.

It is important, however, not to overestimate steric conditions as a kinetic factor in ion-exchange catalysis. Thus, disaccharides show widely different rates of hydrolysis despite the fact that the geometrical conditions of the reaction are practically identical in all cases. Saccharose, in which the C–O–C bond joining the monosaccharide residues is less stable than in its isomers, is hydrolysed 100 times faster than maltose and cellobiose on KPS-200 resin[13].

Inert solvents can have a profound effect on the rate of hydrolysis. The rate constants for the hydrolysis of ethyl acetate[27] and acetanilide[42] in aqueous acetone solutions decrease as the mole fraction of acetone increases. We must assume that the inhibition of the reaction by increased concentration of organic solvent is due not only to the lowering in dielectric constant but also to the different distribution of reactant molecules between the solid and the liquid phase. As the concentration of acetone increases, the relative amount of water absorbed by the resin also increases, and this effect hinders the penetration of relatively insoluble compounds into the resin. Bolton and Henshall[42] conclude, from their experimental results, that sparingly soluble compounds are most efficiently hydrolysed in the presence of the minimum amount of organic solvent required for their dissolution. The relationship between the reaction rate and the dielectric properties of the medium is not always unequivocal. For example, the rate of hydrolysis of dimethyl sebacate in water–dioxan and water–acetone solutions in the presence of KU-2 cation exchange resin goes through a maximum on varying the ratio of water to organic solvent[32].

The influence of the organic solvent on the efficiency (as defined by Hammett) of the resin catalyst was discussed at length in our previous review[1]. In aqueous solutions the efficiency of resins with an intermediate degree of cross-linking towards the hydrolysis of acetates[7] and of ethyl acetoacetate[31] is in excess of unity. The efficiency of a strongly cross-linked cation exchange resin[22] towards the hydrolysis of methyl acetate is well below unity, probably as a result of diffusional limitations.

Reactants having large molecules are particularly sensitive to changes in the content of bridging component. The hydrolysis of Sarin[37] was used to demonstrate the rapid increase in rate constant accompanying a decrease in the divinylbenzene content of the resin from 8 to 1%. It was shown that the catalytic activity of the weakly cross-linked cation exchange resin is comparable to that of soluble acids.

Many workers have examined the influence of the resin particle size on the reaction kinetics in order to throw light on the role of diffusional limitation. The hydrolysis rate constants of ethyl acetate[25] and acetamide[43] are practically independent of particle size over quite a wide range: the rate-limiting step in these reactions is the chemical act itself.

Kinetic effects arising from inner diffusion are very clearly observed when the reactant molecules are very large or branched. Hydrolysis of saccharose under static[18] or dynamic[23,38] conditions is much faster when smaller resin particles are used: Reed and Dranoff[23] have observed a linear relationship between the rate constant and the catalyst particle size. In the hydrolysis of Sarin[37] the kinetic curves become steeper as the diameter of the catalyst particles decreases and as the temperature increases.

The calculated activation energy for the hydrolysis of Sarin on Amberlite-IR 100 is relatively low (5500 cal mole^{-1}). This is additional evidence in favour of rate limitation by inner diffusion. However, the same reaction in the presence of Dowex-50, which has a more open three-dimensional network, gave an activation energy of 11200 cal mole^{-1}, and closely similar values were obtained for the hydrolysis of ethyl acetate[27] and dimethyl sebacate[32].

The rate of hydrolysis of Sarin[37] on Dowex-50 cation exchange resin is insensitive to stirring rate. On the other hand, with a more active catalyst (Amberlite-IRA 400) the rate constant at 20° was 5.3, 7.5, and 8.5 h^{-1} at 60, 800, and 1000 revolutions min^{-1} respectively, suggesting that film diffusion was the rate-limiting step.

Thus, the mechanism of the rate-limiting step depends on the nature of the catalyst.

2. Hydration Reactions

The hydration of organic compounds has been investigated, like their hydrolysis, under static conditions[44] or in a flow system[45].

The hydration of unsaturated hydrocarbons, which gives rise to a system of immiscible liquids, presents some practical difficulties. Effective contact between the reactants and the catalyst is obtained by specially pretreating the cation exchange resin[54] or by homogenising the liquid phase with a suitable solvent or emulsifier[46–48]. Much better yields are obtained in the conversion of hydrocarbons into alcohols by using mixed gas–liquid processes, in which the reaction takes place in a thin layer of water surrounding the resin particles, whilst the reaction products are continuously removed by an excess of water[45].

The writer and Kozlova[44] have increased the equilibrium conversion of tertiary pentenes in the hydration of the pentane–pentene fraction by using a large excess of water and keeping the catalyst (KU-2 cation exchange resin) at the boundary between the liquid phases in a hydrophobic state, obtained by replacing part of the hydrogen counterions by trioctylamine[49]. The reactor was of stainless steel, and fitted with a stirrer. It is interesting to note that the

achievement of equilibrium was accelerated by the addition of anion exchangers: the mechanism was probably analogous to that of the hydrolysis of saccharose[33]. The use of a hydrophobic cation exchanger raised the conversion of tertiary pentenes from 2.7 to 13% (as compared with the previously recommended method[50]).

In the development of apparatus for the continuous production of tertiary butanol by the conversion of isobutene in high yields it has been necessary to abandon the countercurrent principle[51]. It is stated that the best contact between the reactants and the most complete conversion are obtained by a downward flow of water and isobutene through a layer of resin.

Ion exchange resins have been used for the hydration of the following compounds: tertiary pentenes[44,46] (KU-1, KU-2), 2-methylpent-1-ene[46] (KU-1), 2-dioxymethylnorbornene-5[52] (Dowex-50), acetylene[53] (KU-2), hydrocarbons with double and triple bonds[54] (Allasion CS), propene oxide[11] (KU-2. phosphate resins), and hydrocarbons with lactone rings[55] (Amberlite-IRA 400).

Hydration in the presence of a cation exchanger in the hydrogen form is believed to involve the formation of an intermediate carbonium ion[1]. Sulphonated resins are almost invariably chosen, but phosphate and even carboxylate resins can be used for the hydration of reactive materials[11] such as propene oxide. Cation exchange resins in the Hg form are used as catalysts for the Kucherov reaction[53,54]. In view of the conditions used in their preparation, these catalysts are likely to contain H^+ counterions; hence, it is interesting to examine the effect of various counterions on the catalytic activity of the resin. A group of Roumanian workers has shown that in the presence of CS-1 resin in the Cu, Zn, or Cd form acetylene undergoes polymerisation rather than hydration[56].

Cation exchange resins suffer changes of various types when used in practice as hydration catalysts. Firstly, changes in the degree of swelling under the influence of the reactants or of the heat of reaction can lead to disintegration of the particles[1]. An interesting way of guarding against these effects is to use coarsely granular[57] or two-phase[21] cation exchange resins. Secondly, blocking of the active groups in the resin may occur as a result of the incorporation of reactant[58] or product[11] molecules. Thirdly, irreversible chemical reactions (e.g. desulphonation) can proceed within the resin at high temperatures. The writer and Tulupov have shown[58-60] that this reaction can be vigorous in aqueous, alcoholic, and other media, particularly at high temperatures and when the heat of reaction is large. Thermal desulphonation and other forms of ageing of the resin lower the yield of hydration products[45].

The thermal stability and catalytic activity of sulphonated cation exchange resins in hydration reactions depend on the structure of the polymer network. In many reactions the presence of sulphonic acid groups is a necessary but not always sufficient condition for catalytic activity. For example, the hydration of acetylene proceeds smoothly in the presence of the sulphonated cation exchange resin KU-2, but it is not catalysed by the sulphonated phenol–formaldehyde KU-1 resin[53]. Sulphonated asphaltene deposited on silica gel does not catalyse the hydration of tertiary pentenes[61].

The water uptake of the catalyst plays an important role in determining the effectiveness of the catalyst, and sometimes even the course of the main reaction. It has been shown[8] that a KU-2 resin containing $< 24\%$ of water catalyses only the polymerisation of tertiary pentenes. At higher water concentrations the strength of the bond between water molecules and the sulphonic acid groups decreases, and addition of water to the double bond of the hydrocarbon becomes easier. In the presence of a large excess of water the hydration of pentenes is practically quantitative, with a negligible amount of polymerisation[44].

Tertiary pentenes form carbonium ions more readily than other C_5 alkenes: in practice, therefore, they alone can add on water in the presence of KU-2. Normal pentenes, and 3-methylbut-1-ene, remain unchanged[62] even after lengthy treatment at high temperature (75°) with hydrated KU-2 resin. A process for the selective removal of tertiary pentenes from complex mixtures[62] can be based on these properties.

The rate of hydration of alkenes and other sparingly water-soluble compounds can be increased by adding indifferent organic solvents to improve the contact between catalyst and reactants. This principle has been successfully applied in practice[46], but a quantitative relationship between the reaction rate and the nature of the solvent has not yet been derived.

The hydration of alkenes is often accompanied by polymerisation and isomerisation side reactions, also involving a carbonium ion mechanism. Polymer formation has been observed in the hydration of propene[45], isobutene[51], and tertiary pentenes. These side reactions can become predominant under the appropriate experimental conditions[63].

3. Dehydration Reactions

For preparative purposes, dehydration is often carried out as a batch process. When an azeotrope-forming solvent[64] is used, the reactor includes a reflux condenser fitted with a water-separation trap, and the reaction is allowed to continue until the stoichiometric amount of water has been collected. In some cases the organic dehydration product is steam-distilled, thus ensuring that the water content of the resin remains constant and providing relatively mild conditions[65].

Under industrial conditions, dehydration is usually carried out as a continuous process. Soviet workers[66,67] have described a rational pilot-scale process for the production of isobutene which relies on a reactor without heat exchangers in order to minimise energy consumption. Free transport of the materials and a high throughput (1300–1400 kg h^{-1}) were achieved by locating the KU-1 cation exchange resin in the upper part of the reactor[68].

A flow apparatus for studying dehydration kinetics has been described[69]. It includes a continuous sampling facility (a microsyringe for removing samples of the product through a silicone rubber cap).

Resins have been used to dehydrate the following compounds: pentan-1-ol[64] (KU-2), cyclohexanol[70] (KU-2), cyclohexylethanol[71] (KU-2), menthol[72] (sulphonated polyphenyl resin), terpin hydrate[65] (KU-2), dimethylvinylethynyl carbinol[74] (KU-1), methylphenylethanol[73] (KU-2, phosphate exchangers), symmetric alkyne glycols[75] (KU-1), and castor oil[76]. All the cation exchangers were used in their hydrogen form.

There can be no doubt that the use of cheap sulphonated phenol–formaldehyde resins is fully justified, since these materials can extract water from alcohols at temperatures $< 100°$. Under these conditions the exchange capacity and other physicochemical properties of the resin do not change appreciably[60]. At higher temperatures, on the other hand, the loss of capacity of these resins in aqueous[60], alcoholic[60], and hydrocarbon[8] media can be serious.

Thus, the claim by some French workers[77] that sulphonated phenol–formaldehyde resins can be used up to 210° is unacceptable. The KU-2 resin is appreciably more stable[60]: it can be used as a dehydration catalyst up to 150°, or up to 200° if used once only. If the experimental conditions require a reaction temperature in excess of 200°, the recently developed[72] sulphonated polyphenyl cation exchange resins, which have a high thermal stability, should be tried.

Since the catalytically active form of the cation exchange resins is the hydrogen form, the effectiveness of these catalysts is determined primarily by their acidic properties. The writer has shown[78] that the carboxylic acid resin SG-1 does not catalyse the dehydration of t-pentanol. The more acidic, phosphorus-containing RF cation exchanger accelerates this reaction, but the achievement of equilibrium is even faster in the presence of the KU-2 cation exchange resin. The relative activity of the sulphonate and phosphate exchanger was later confirmed[73], and it was shown that in the latter the kinetics of methylphenylethanol dehydration are affected by the structure of the polymer network. Zirconium phosphate was found to be the least active of the phosphorus-containing exchangers.

Water content has a large effect on the activity of cation exchangers. It would appear from the available experimental data that water absorption lowers the catalytic activity of cation exchangers towards the dehydration of compounds with a relatively low molecular weight (e.g. ethanol[69] and t-butanol[79]). In the dehydration of compounds with large or branched molecules, such as terpene alcohols[80], trapped water loosens the three-dimensional network of the cation exchanger and decreases the steric barriers to the formation of carbonium ions, thus leading to faster reaction.

An important controlling factor in dehydration reactions at cation exchangers, which allows control over the nature and yield of the products, is the composition of the medium and in particular the addition of indifferent solvents. Karpov and coworkers[81], who published the only noteworthy data on this subject, stress the importance of careful choice of solvent. Thus, addition of high-boiling hydrocarbon solvents in the preparation of dipentyl ether affects neither the yield nor the rate of the reaction, but if the reaction is carried out in a *p*-xylene medium the yield of ether drops by 17% owing to alkylation of the solvent by the alcohol. For the same reason, addition of xylene is undesirable in the preparation of di-n-octyl ether. On the other hand, addition of n-nonane prevents the complete dehydration of octanol on KU-2 and raises the yield of octyl ether by 29%.

The reaction temperature has a profound effect on the nature of the dehydration products. Shuikin and coworkers[82] have shown, in their study of the dehydration of primary alcohols, that the reaction on KU-2 gives mainly ethers at 135° in 5 h. On raising the temperature and the contact time, the proportion of alkenes in the reaction products increases.

As in the case of homogeneous acid–base catalysis, the rate of dehydration on ion exchangers increases with the concentration of catalytically active ions. The dehydration of t-butanol is faster in the presence of KU-1 resin[83] than in the presence of an equivalent amount of sulphuric acid. According to Helfferich's theory[6], the greater efficiency of the ion exchanger is due to selective absorption of alcohol molecules by the cation exchanger rather than to any difference in catalytic activity between hydrogen ions under homogeneous catalysis and ion-exchange catalysis conditions respectively. Unfortunately, no data are given[83] on the distribution of the alcohol between the liquid phase and the catalyst.

Soviet workers have shown that the catalytic activity of sulphuric acid and of sulphonated polystyrene resin towards the dehydration of tetracycline is determined only by value of the Hammett acidity function and is independent (within the range explored) of the concentration of water, divinylbenzene, and third component (Na^+ ions) in the resin[84]. As Fig. 1 shows, all the points in the experimental plot of the logarithm of the rate constant for this reaction against the acidity function lie on the same straight line. This is evidence that the catalytic activity of the H^+ ions is the same in the resin and in the acid phase. It would be interesting to extend these results[84] to reactions whose kinetics depend on the distribution of reactants between the liquid phase and the cation exchanger.

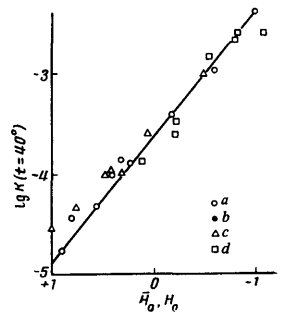


Figure 1. Logarithm of the rate constant for the dehydration of tetracycline plotted against the acidity function in the presence of: *a*) H_2SO_4; *b*) ion exchanger in the mixed Na–H–T form; *c*) ion exchanger in the T–H form; *d*) ion exchanger in the T–H form, dried to a known water content (T = tetracycline)

Detailed kinetic studies of the dehydration of tetracycline[85], ethanol[69], and dimethylethanol[79,83] have been published.

4. Synthesis of Esters

Esters are prepared mostly by esterification and ester interchange (transesterification) reactions. In order to avoid the formation of water and thus to raise the yield of esters, anhydrides are sometimes added with the alcohol[86,87], and alkenes[88], ethylene oxide[89], or ethylene carbonate[90] with the acid.

Like the reactions discussed above, esterification can be carried out as a batch process or as a continuous process. A simple version of the laboratory apparatus for the continuous production of ethyl octanoate[91] is shown in Fig. 2. The mixture of reactants in a known molar ratio, and containing hydroquinone as a polymerisation inhibitor, is supplied by the metering pump *2* to the bottom of a temperature-controlled glass reactor *4* of the "double tube" type, packed with KU-1 resin swelled in the reaction mixture. The vapours of ethyl octanoate, ethanol, and water, formed in the reactor at the boiling point of the reaction mixture, are continuously condensed (*6*) and collected in the receiver *7*.

Trofimov and Isagulyants[92] have described a relatively simple, high-capacity reactor for the continuous production on an industrial scale of n-nonyl methacrylate by the transesterification of methyl methacrylate.

Ion exchangers have been used to esterify formic acid with ethanol[93] (KU-2), acetic acid with ethanol[94] (KU-2), butanol[95] (KU-2), isobutanol[95] (KU-2), and pentanol[96] (KU-2), acrylic acid with ethanol[91], methacrylic acid with C_5–C_{10} aliphatic alcohols (KU-2) and ethanediol[98] (SBS, SDV-3), naphthenic acids with ethanediol[99] (KU-2), adipic acid with methanol[100] (KU-2) and higher aliphatic alcohols[101] (KU-2) as well as ethanediol[86] (silicone cation exchange resin), sebacic acid with allyl alcohol[102] (KU-2), benzoic acid with ethanediol[103] (KU-1), salicylic acid with aliphatic alcohols[104] (KU-2), maleic acid with allyl alcohol[102] (KU-2), terephthalic acid with methanol[105] (Wofatit KPS-200), and sorbic acid with aliphatic alcohols[106] (KU-2). Furthermore, esters have been prepared by the reaction between maleic anhydride and butanol[107] (KU-2), phthalic anhydride and glycerol[86] (silicone cation exchange resin), and methyl methacrylate and n-nonanol[92] (KU-2).

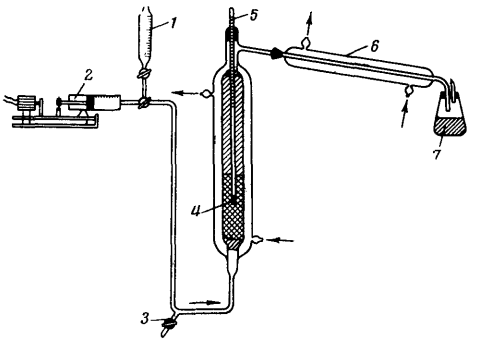


Figure 2. Laboratory apparatus for the continuous esterification of acrylic acid with ethanol

Since many of these esters are produced on an industrial scale, the use of ion-exchange catalysis should now be regarded not merely as an elegant preparative technique but also as a potential method in modern chemical technology, combining simplicity in the design and operation of the plant with high yields of valuable products.

In addition to the traditional hydrogen form, salt forms of sulphonated cation exchangers[108,109], which behave as Lewis acids, are used in the catalytic synthesis of esters. Because of their high thermal stability in the salt form[110], these resins can be used to accelerate reactions taking place at temperatures of 200° or higher. Sulphonated cation exchangers in the hydrogen form on a silicone substrate are also interesting in this respect[86]. Macroporous cation exchangers—about whose catalytic activity very little is yet known—offer the prospect of accelerating esterification reactions involving large molecules.

It should be noted that the nature of the polymer network of the resin has practically no effect on the yield of the ester[107] or on the kinetics of the reaction between low-molecular-weight acids and alcohols[16]. However, if one of the reactants has a high molecular weight the structure of the three-dimensional network becomes an important kinetic factor: some interesting comparisons have been reported[111,112] of various sulphonated cation exchangers as catalysts for the synthesis of butyl oleate and polyesters. Cation exchangers containing carboxyl groups are said[111] to have little effect on the rate of these esterifications.

On increasing the amount of cation exchanger the yield of ester, as a rule, increases to a limiting value and thereafter remains constant[96,104,113]. However, in the esterification of methacrylic acid with higher alcohols[114] the yield of ester goes through a maximum at 10 wt.% of catalyst. Unfortunately, the results of different authors are often difficult to compare because different units are used to define the amount of catalyst added. The writer suggests the adoption of mg-equiv. of active groups per g-equiv. of acid or alcohol as a universal scale: these units are particularly useful in kinetic studies.

Rate constants referred to 1 mg-equiv. of active groups give a clear indication of the specific features of the catalyst and are to be preferred to the traditional quantities used in formal kinetics. The rate constants for the esterification of glycerol by acetic acid, referred to 1 g of KU-1 and KU-2 resins, have been reported[115] as 1.65×10^{-4} and 4.29×10^{-4} min^{-1} respectively. When referred to 1 mg-equiv. of active groups these constants become practically indistinguishable (4.0×10^{-4} and 3.9×10^{-4} min^{-1}), which is consistent with the lack of a specific effect of the network structure under these particular conditions.

Table 1. Influence of particle size and cross-linking of KU-2 ion exchanger on the rate of esterification of acetic acid by ethanol

Particle size, mm	Reaction rate, $\frac{g\ CH_3COOH}{s \cdot g\ KU\text{-}2} \times 10^4$			
	1% devinylbenzene		20% divinylbenzene	
	liquid-phase reaction	vapour-phase reaction	liquid-phase reaction	vapour-phase reaction
0.5–1.0	53	16.2	11	9.8
0.1–0.25	58	34.5	—	13.7
0.01–0.10	67	85.8	18	20.5

If the rate of esterification is limited only by the reaction itself, and diffusional limitations are negligible, the reaction rate is independent of the stirring rate[116,117] and of the size of the resin particles[116–118]. As inner diffusion effects become predominant, the size of the catalyst particles begins to influence the rate of esterification. Table 1 shows the effect of this factor and of the degree of cross-linking of the KU-2 exchanger on the rate of esterification of acetic acid by ethanol in the liquid[94] and the vapour[119] phase (for 15–20% conversion).

It is evident from Table 1 that the influence of particle size on the rate of esterification of acetic acid by ethanol is appreciable even in the liquid phase. In the vapour phase the effect is more marked because the swelling of the catalyst is minimal. As expected, the reaction is faster on the strongly swelled KU-2 cation exchanger containing 1% of divinylbenzene than on the resin with 20% of cross-linking agent. Very large reactant molecules can interact by topochemical reactions: in this case the effect of particle size is even more marked[1]. In a very few

cases (e.g. the esterification of glycerol by phthalic anhydride and talloleic acid[86]) the cation exchanger does not accelerate the reaction, evidently because of inactivation of the exchanger by alkyd resins.

The rate of esterification decreases substantially when the chain length of the aliphatic radical in the alcohol[104] or the acid[120] is increased: the analogous relationship for homogeneous acid–base catalysis was established by Menshutkin[121] at the end of the last century. The influence of this factor on the esterification kinetics is less marked at elevated temperatures[122].

The yield of esters is a function of the structure of the reactants. Normal alcohols give esters in higher yields than their isomers. The accurate correlation between the yield of ester and the molecular weight of the alcohol, which had been established[123] for homogeneous reactions at equilibrium, does not hold in the presence of ion exchange catalysts[97]. On raising the molecular weight of aliphatic acids up to C_5 the yield of isopentyl esters remains constant[120], but with still larger acid molecules the yield begins to decrease. This effect is probably associated with side reactions, or with the preparative difficulty of isolating the esters of higher acids, rather than with any thermodynamic feature of the esterification reaction.

Some workers[96] lower the temperature of the reaction mixture by adding low-boiling solvents in order to minimise side reactions. However, this expedient also lowers the rate of the main reaction, and it is necessary to reach a compromise and accept solvents of relatively high boiling point. In particular, the esterification of ethanediol by naphthenic acids and of pentanol by salicylic acid gives higher yields[99,104] in boiling xylene than if toluene is used to remove the water azeotropically.

The yield of esters[124] and the reaction kinetics[120,122] are very sensitive to the molar ratio of alcohol to acid. Esterification in the presence of an excess of alcohol produces conditions leading to resin swelling, which accelerate the reaction[120,122]. On the other hand, in the presence of an excess of carboxylic acids the resins do not swell appreciably and the reaction is slower than when the reactants are taken in equimolecular proportions.

It does not follow, however, that a chemical reaction is invariably accelerated by increasing the degree of swelling of the resin. The water evolved in the liquid-phase esterification of acetic acid by ethanol accentuates the swelling of the cation exchanger, but the rate constant of the reaction falls off[94]. In the esterification of salicylic acid by methanol, increased water concentration in the reaction mixture tends to inhibit the reaction[117]: the author[117] correctly ascribes this effect to partial deactivation of the protons in the sulphonic acid groups by hydration, as a result of which the formation of active intermediate complexes is sterically hindered.

Esterification is often accompanied by side reactions which (like the main reaction) involve the participation of a carbonium ion: dehydration of the alcohol[104,120] and polymerisation of the resulting alkenes[120], alkylation of the solvent[104], and dehydration of the ester[122].

The adoption of ion-exchange catalysis in industrial synthesis is economically justified[96]. According to Chashchin and coworkers[124], a saving of 10–20 roubles per tonne of butyl acetate could be made by replacing the soluble catalysts by ion exchangers.

5. Alkylation

Like the reactions already discussed, alkylation can be carried out as a batch process or as a continuous process. The use of a fluidised bed of catalyst by Belov and Isagulyants[125] is particularly interesting.

Ion exchangers have been used as catalysts for the alkylation of *p*-xylene by propene[126], *o*-xylene by isobutanol[127] (KU-2), phenol by propene[128] (KU-2), isobutene[129], and pentenes[130] (Ku-2), and by 2-ethylhex-1-ene[131] (SDV-3), propene trimer[132] (Amberlist-15), isoprene[133] (KU-2), monoarylacetylenes[134] (sulphonated cation exchanger), α-pinene[135] (KU-2), isobutanol[136], higher aliphatic alcohols[137] (KU-2), and benzyl alcohol[138] (KU-2); also for the alkylation of *p*-cresol by isobutene[139] (KU-2), cyclohexene[140] (KU-2), styrene[141] (KU-2), octanol[142] (KU-2), and cyclohexanol[140] (KU-2), for the alkylation of *o*-xylenol by hex-2-ene[143] (KU-2), cyclohexene[143] (KU-2), and styrene[144] (KU-2) of β-naphthol by isobutanol and butanol[145] (KU-2), of pyrocatechol by but-1-ene[146] «Allasion CS» and isobutene[147] (KU-2), of hydroquinone by isobutene[148] (KU-2), of guaiacol by hex-1-ene[149] (KU-2), and of *p*-methoxyphenol by alkenes[150] (KU-2).

The main reaction in the alkylation of phenols is direct replacement of hydrogen in the benzene nucleus, leading in most cases to the formation of monoalkylphenols: the substitution occurs mostly in the *p*-position to the phenolic hydroxyl, or (if this position is occupied) in the *o*-position[142]. Dialkyl phenols are sometimes formed in addition to the monosubstituted phenols. In the presence of a large excess of alkylating agent the disubstituted phenol may account for most of the yield[143,144]. Some workers have observed the formation of alkyl phenyl ethers, which usually[140,151] but not invariably[140] undergo regrouping into alkylphenols. Some reactions are complicated by the disproportionation of the alkylphenols[152], the replacement of one alkyl radical by another[152], the degradation of branching side-chains[153], and polymerisation of the hydrocarbons[144,152]. The yield of dialkyl substituted phenols decreases as the molar ratio of phenol to alkylating agent increases[125,138,148,154,155] and also if the reaction time is extended[155]. Other conditions being the same, the yield of dialkylphenols on cation exchangers is less than in the presence of soluble acids[155], which suggests selective sorption of the phenols from the reaction mixture[154].

The nature of the reactants has a considerable influence on the total yield of alkylation products. Increasing the number of substituents in the nucleus of the compound to be alkylated, and branching of the hydrocarbon chain of the alkylating agent, produce a lower yield of alkylphenols[153]. Soviet workers[153] have convincingly demonstrated, by studying the alkylation of the cresol and xylenol isomers, steric hindrance to the entry of a tertiary radical in the *o*-position to the methyl or hydroxyl group of a phenol. This *ortho*-effect is most marked in symm.*o*-xylenol, which is not alkylated by di-isobutene: the t-octyl radical (6.18 Å in diameter) cannot be located between two methyl groups or between a methyl and a hydroxyl group, whose separation is 5.24 and 5.17 Å respectively[157].

Information on the influence of the cation exchanger on alkylation reactions is mostly qualitative[141], and is so scanty that useful generalisations cannot be made.

More definite conclusions are possible on the effect of water content of the catalyst on the yield of alkylation products. The yield of alkylphenol on KU-1 resin containing 20–30% of water is 50% lower than on the same resin dried to constant weight[158]. Alkylation of phenol on SDMS resin prepared by sulphonation of shredded rubber[159] and having a water content of 20% gave a 69% yield of octylphenol. On decreasing the water content to 9% the yield rose to 75%, and on a dry resin the yield reached 80%. The highest yield of bis-phenols by the reaction of phenol with

diarylalkynes[134] was obtained at 2% water content of the cation exchanger. From these results, pre-drying of ion-exchange alkylation catalysts in an air oven at 110–120° is recommended. Alternatively, the resin may be dried in a vacuum or by refluxing with an azeotropic solvent (e.g. benzene).

If the alkylation involves not only the surface but also the bulk of the resin particles, smaller particle size raises the yield of dialkyl derivatives. Soviet workers have given a convincing explanation of this effect[154] by pointing out that the molar ratio of phenol to alkylating agent is greater in the cation exchanger than in the bulk of the solution: this favours the formation of monoalkyl derivatives. When the particle size of the resin is decreased the relative importance of the reaction taking place at the surface (and therefore at the same molar ratio of components as in the reaction mixture) increases, and so also does the yield of dialkylphenol.

In some cases it is useful (or even necessary) to operate at elevated temperatures in order to increase the rate of diffusion of reactants within the resin particles and the mobility of the counterions of the active groups as well as accelerating the reaction itself. However, an excessive rise in temperature may cause dealkylation and favour side reactions as well as irreversible changes in the catalyst. Thus, on raising the temperature of the alkylation of phenol by di-isobutene in the presence of the cation exchanger SDMS the yield of alkylphenol increases up to 100°, remains constant in the range 100–115°, and falls off above 120° due to the onset of dealkylation[159]. When phenol is alkylated with high-molecular-weight alkenes, the total yield of alkylphenol rises from 64 to 81% as the temperature is increased from 150 to 160°.[160] However, whereas at 130° only monoalkylphenols are formed, the product obtained at 150° appears to contain (judging by its boiling range) di- and even polyalkylphenols.

Special caution is necessary when using sulphonated phenol–formaldehyde cation exchangers at high temperatures. The KU-1 resin is so unstable towards heat that the yield of useful product decreases by a factor of two[141] when the resin has been used three times as a catalyst for the aryl-alkylation of *p*-cresol at 110°. Under the same conditions the KU-2 resin retains its catalytic properties unchanged for at least 12 consecutive operations, and has been used for 500–600 h without regeneration[153] in the continuous alkylation of phenols at 120°. Under the more stringent conditions of the alkylation of asymm.*o*-xylenol by alkenes[143], the exchange capacity of KU-2 fell from 4.9 to 2.3 mg-equiv. g^{-1} after 13 reaction cycles.

The catalytic properties and technological potential of cation exchangers in alkylation reactions are affected not only by changes in exchange capacity but also by the extent of swelling in the reaction medium[161], resinification of the surface[161,162], and breaking up of the particles[163]. Resinification of the surface can be avoided by adding indifferent solvents, and its effects can be cured by regenerating the cation exchanger. Regeneration can be achieved in the cold or by refluxing with resin solvents such as acetone[143], ethanol[154], benzene[161], or an alcohol–benzene mixture[153]. Some authors recommend successive treatment of the resin in alkali and hydrochloric acid[143] (or 10% sulphuric acid[135]) after the treatment with organic solvents.

The mechanism of the reaction is generally considered to be a nucleophilic addition through a reactive intermediate state (π-complex or carbonium ion[136,164,165]).

This mechanism has recently been confirmed by Soviet workers[153] by measurements of the electrical conductivity of mixtures of phenol, KU-2 resin, and the trimer of propene.

6. Polymerisation and Isomerisation Reactions

These reactions can be carried out as batch processes at high pressure in stirred autoclaves[166], but semi-continuous[167] or continuous[168] methods are usually employed. The continuous method sometimes offers higher yields[167] as well as the other advantages of continuous operation.

Ion-exchange resins have been used as catalysts for the dimerisation and trimerisation of alkenes[166,168] and acetaldehyde[167] (KU-2), and also for the polymerisation of vinylbenzene[169], isobutyl vinyl ether[170], and acetaldehyde[171] (various sulphonated resins). Ion exchangers have also been used as catalysts for the isomerisation of alkenes[62,72,172,173] (sulphonated cation exchangers), unsaturated alcohols[54] ("Allasion CS"), hydrocarbons (Wofatit L-150)[174], phenol esters[175] (KU-2), cyclohexanoneoxime[176] and phenylhydrazones[3] (resins of the KU-2 type).

Often polymerisation, isomerisation, and cracking occur together, and the reaction product is complex and variable in composition. In most cases these reactions are accelerated by cation exchangers in the H form, but a resin containing mercury counterions has been used[54] for the isomerisation of propynols. The isomerisation of glucose is accelerated by anion exchangers in the OH form[174].

In the low-temperature polymerisation of oxygen-containing compounds the main factor leading to loss of catalytic activity is the blocking of reactive sites by the reaction products, which hinders the contact between the counterions and reactant molecules[170]. Impurities in the monomer contribute to the deactivation of the catalyst: hence, special attention must be devoted to the purification of the raw materials.

If the isomerisation can proceed at temperatures up to 80–90°, sulphonated phenol–formaldehyde cation exchangers can be used without serious loss of catalytic activity. Thus, after 99, 477, and 1600 h operation at 75–80°, samples of KU-1 gave 83, 78, and 76% conversion of 2-methylpent-1-ene and 2-methylpent-2-ene, the selectivity remaining constant[168]. A cation exchanger of higher thermal stability (e.g. KU-2) must be used for the di- and trimerisation of alkenes, which usually require temperatures in excess of 100°.

The effect of temperature on the yield of polymerisation and isomerisation products depends on the nature of the reactants, on the reversibility of the reaction, on the reaction time, and on the moisture content of the resin[177–180].

The possibility of a reaction is often determined by the nature of the active groups and by the geometry of the three-dimensional network of the resin. For example, it is well known that carboxylate and phosphate cation exchangers do not catalyse the polymerisation of isobutene[177]. Sulphonated polyphenyl cation exchangers[72] are efficient catalysts for the isomerisation of but-1-ene to but-2-ene, and for the same reason a phosphoric acid polyelectrolyte has a negligible effect on the rate of this reaction. The KU-2 resin is a more effective catalyst than hydrochloric acid for the pinacoline rearrangement[181], and the polymeric carboxylate cation exchanger KB-4P-2 does not affect the rate of isomerisation.

However, these reactions are not accelerated by any sulphonated cation exchanger in any physical state. For example, a technical mixture of KU-1 and another sulphonated phenol–formaldehyde cation exchanger does not cata-

lyse the polymerisation of tertiary pentenes[182] and isobutene[177]. Within limits, the activity of a cation exchanger can be altered by modifying the state of the resin. Thus, by finely dividing the dried KU-1 resin or by loosening its network with water or methanol it is possible to bring about a very significant increase in its catalytic activity towards the polymerisation of tertiary pentenes. However, if the finely divided exchanger is heated in the air or in nitrogen atmosphere it ceases to be a catalyst for this reaction[182]. The more ordered network of the polymeric KU-2 catalyst is sufficiently open even under dry conditions to permit diffusion of low-molecular-weight alkenes such as isobutene[170], tertiary pentenes[178], and α-methylstyrene[73]. In this case the polymerisation proceeds faster on the dried than on the hydrated resin. The KU-2 catalyst is more active towards the formation of high polymers when in the hydrated state[80], since a very open three-dimensional network is needed to allow the interlinking of a large number of monomer units.

The step which controls the reaction kinetics depends on the water content of the cation exchanger. In the pinacoline rearrangement, carried out in the presence of KU-2 resin swelled to the limit, the rate-limiting step is the chemical reaction itself[181], because the diffusion of pinacone is unhindered when the resin particle is swelled by water. Diffusional limitation begins to be appreciable in the polymerisation of t-pentenes on dried KU-2 resin, and therefore the rate of this reaction decreases as the size of the catalyst particles increases. Fang[10] obtained a similar somewhat unexpected result in his work on the kinetics of isomerisation of $(d+)$-α-isobutyldesoxybenzoin on a macroporous cation exchanger in which practically all the sulphonic acid groups of its enormous internal surface were available for the formation of carbonium ions.

Fang[10] used the change in the rate constant for the racemisation of $(d+)$-α-isobutyldesoxybenzoin as a measure of the stability of the catalyst (Amberlist-15) towards heating in an inert medium at 100–165°. This is the first example of the use of a kinetic quantity to characterise the thermal stability of a resin. These results are shown in Table 2 as rate constants referred to 1 g of catalyst (k_1) or 1 mg-equiv. of active groups (k_2).

Table 2. Influence of heat treatment on the catalytic activity of Amberlist-15

Temp. of heat treatment, °C	Exchange capacity of resin, mg-equiv. g^{-1}	Rate constants, min^{-1}	
		$k_1 \times 10^4$	$k_2 \times 10^4$
100	4.61	5.33	1.16
110	4.55	5.07	1.11
120	4.55	5.00	1.10
130	4.48	5.09	1.14
140	4.30	4.81	1.12
150	4.07	3.53	0.87
165	4.36	3.42	1.02

It can be seen from Table 2 that heat treatment of the cation exchanger at temperatures up to 140° leads to partial desulphonation with a corresponding decrease in k_1, whilst k_2 remains approximately constant. At still higher temperatures both rate constants decrease, since the access of ketone molecules to the active centres is hindered by the shrinkage of the three-dimensional network of the resin.

These views have long been held by the present writer in connection with the thermal stability of ion exchangers[183]: their relevance to ion-exchange catalysis is now beginning to be appreciated.

As in the case of other Brønsted acids[184], polymerisation in the presence of ion exchangers occurs by a cationic mechanism[185]. Intermediate formation of a carbonium ion is suggested during the isomerisation of l-menthene[72], and this mechanism has been proved beyond doubt for the transformation of but-1-ene into but-2-ene (which was investigated by the isotope exchange method[24]).

7. Condensation Reactions

Additional evidence of the advantages of ion exchange catalysis over the classical methods relying on soluble acids or alkalis has become available as a result of the current interest in condensation reactions brought about by ion-exchange resins.

Many reactions take place under milder conditions in the presence of ion exchangers, giving a higher grade of product[186,187] in better yields[188]. Because of the improved quality of the technical products obtained by ion-exchange catalysis, some purification stages can be omitted (for example, extraction in the preparation of polyhydric alcohols[187] or neutralisation in the preparation of diacetone alcohol[189]), and therefore the process can be speeded up on the industrial as well as on the laboratory scale. Thus, the preparation of diacetone alcohol by the condensation of acetone in the presence of barium hydroxide requires 120 h as compared with 8–10 h if an anion exchanger is used[189].

In some cases the use of ion exchangers offers new possibilities in organic synthesis. A striking example of this is the cyanoethylation of water in the presence of AV-16 anion exchanger, achieved by Mekhtiev and coworkers[190], which is impossible under homogeneous acid–base catalysis conditions.

The advantages of ion-exchange catalysis have led many authors[187,191–193] to suggest the use of ion exchangers as condensation catalysts on a pilot-plant scale and even on a full industrial scale.

Like the reactions already discussed, condensation can be carried out as a batch process or a continuous process. However, a combined approach is used for the synthesis of trimethoxypropane because the reaction mixture tends to separate into layers in the continuous reactor, causing low yield[187].

Most of the recent work in this field has been concerned with the use of ion exchangers as catalysts for cyanoethylation[4,194–197] (anion exchangers), aldol condensation[103,187,189,198,199] (anion exchangers, and occasionally cation exchangers), the Prince reaction[192,200–203] (cation exchangers), and the reaction between aldehydes and alcohols[103,204–208]. Some papers have dealt with the Knoevenagel condensation[209] (Dowex-3) and the reactions of phenol with acetone[191] and acetylene[210] (cation exchangers), the reactions of nitromethane with furfural[211] and paraformaldehyde[212] (anion exchangers), of acetic anhydride with hydrogen sulphide[193] and sugars[213], of cyclohexene with hydrogen peroxide[214] (KU-2), of various phenols with 1,3-cyclohexadiene[215] (Dowex-50), of oleic acid with diethylenetriamine[216]. Among the areas where further research is needed we could mention hydroxylation reactions[214], the synthesis of nitro derivatives[217,218] and the hitherto unpromising condensation of ketones with alcohols to give the corresponding acetals[206].

Although ion-exchange catalysts in general offer a higher selectivity than soluble acids and alkalis, this feature should not be overstated[187,195,219,220]. Very careful selection of the optimum conditions is necessary to minimise side reactions. Parameters such as reaction temperature, contact time, and molar ratios of components must be varied, as well as the water content, amount, and nature of the resin (ionic strength of the active groups, structure of polymer network, degree of cross-linking). As an illustration, the effect of various parameters on the yield of the cyanoethylation of ethanethiol[221] is shown in Fig. 3. It is evident that the yield of β-(ethylmercapto)propionitrile, calculated on the basis of acrylonitrile consumed, is not a sensitive function of the reaction conditions. On the other hand, the yield calculated on the basis of added acrylonitrile varies widely with the conditions of the reaction, and this behaviour must be taken into account in optimising the process.

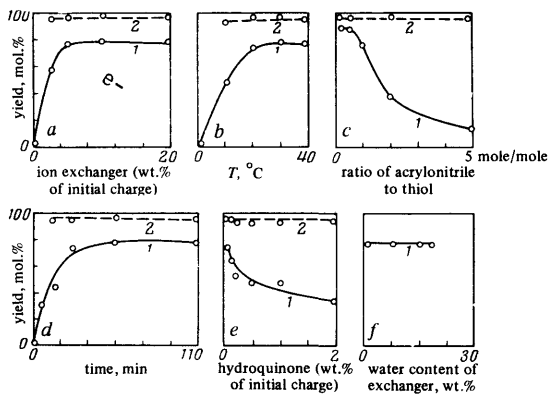


Figure 3. Effect of various parameters on the yield of the cyanoethylation of ethanethiol, expressed in terms of acrylonitrile (AN) added (*1*) and consumed (*2*): *a*) amount of AV-16 anion exchanger; *b*) temperature; *c*) AN : thiol molar ratio; *d*) time of experiment; *e*) amount of hydroquinone added; *f*) water content of resin

With the exception of the condensation of phenol with acetylene[210], catalysed by a resin in the Hg form, cation exchangers are commonly used as catalysts in the H form, and anion exchangers in the OH form, though an anion exchanger in the acetate form has been used[209] in the Knoevenagel condensation. The activity of the cation exchangers towards the condensation of phenol with acetone[191,222] can be increased by the addition of promoters: thioglycollic acid, ethanethiol, and others. A very ingenious method has been devised[222] to improve the quality of the diphenylolpropane obtained catalytically: 3–20% of the sulphonate groups in the cation exchanger are esterified with thiols instead of adding promoters to the reaction mixture.

The effectiveness of anion exchangers increases with their basicity, and improved yields can sometimes be obtained in this way. In some cases, however, weakly basic anion exchangers give better results (e.g. in the synthesis of thioglycollic acid[193]), and in some reactions (aldol condensation of acetaldehyde[1]) their use is mandatory.

Sulphonated cation exchangers are most frequently used in reactions which occur through the formation of an intermediate complex cation. In some reactions[197], adequate activity is obtained with phosphate or carboxylate resins, the latter being the more active.

Several examples have been reported[191,208,223] of the superiority of sulphonated polystyrene cation exchangers as compared with various sulphonated phenol–formaldehyde resins, all of which have a more compact three-dimensional network. Some compounds, such as diphenylolpropane, are formed only on KU-2 cation exchanger: the KU-1 resin merely absorbs phenol and acetone in molar proportions without inducing condensation.

In the presence of water, the activity of the catalyst can remain unchanged[198], it can increase[205], or it can even decrease[191]. Hence, the exchanger may have to be hydrated, or it may have to be dried, before the reaction.

Dehydration, like other forms of heat treatment, is relatively safe with cation exchangers of the sulphonated polystyrene type. Thus, KU-2 cation exchanger can be used for 1200 h without regeneration[222] in the synthesis of diphenylolpropane at 75°. Its analogue (Dowex-50) remained active for several years[206] under milder conditions in the condensation of acetone with alcohols.

Strongly basic anion exchangers in the OH form are sensitive to heat, and their exchange capacity rapidly decreases[224] on drying the resins even at ordinary temperature. Hence, the deactivation of the AV-17 anion exchanger towards condensation reactions reported by Isagulyants and coworkers[217,225] is not surprising. The relationship between the thermal stability and the catalytic activity of anion exchangers has not so far been investigated.

Published work on the condensation kinetics has dealt with the effect on the reaction rate of indifferent solvents[226], of the particle size[227], and degree of cross-linking of the resin[191], and of the nature of the active groups[228]. The activation energy[195,221,227,229] and the kinetic order of some condensation reactions have been reported[195,200,209,221,230]. An anomalously low activation energy has been observed[229] in the aldol condensation of acetone (4.5 kcal mole^{-1}), pointing to inner diffusion as the rate-limiting step. The kinetic order of the reaction on ion exchangers may not be the same as in homogeneous acid–base catalysis[200]; in the condensation of chloroacetaldehyde with polyhydric alcohols[230] the kinetic order depends on the amount of KU-1 present and on the molar ratio of the reactants. This fact underlines the specific features of ion-exchange catalysis, which goes beyond the simple idea of "a homogeneous phase in which the reaction can take place".[6]

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The period in the development of ion-exchange catalysis which we have discussed is qualitatively different from the previous stage. Between 1961 and 1968, satisfactory theoretical foundations were developed and new ideas were put forward (for example, on the blocking of ion exchangers) in the form of precise quantitative relationships. Kinetic studies have attracted much more attention than during the previous stage, and have helped to reveal the specific features of ion-exchange catalysis. Considerable progress has been made in the synthesis and exploitation of new (thermally stable, macroporous, and mixed) ion-exchange catalysts which enable many of the defects of the older ion-exchange materials to be overcome or at least mitigated. The relationship between thermal stability and catalytic activity has been formulated in principle; these

basic ideas are of the utmost importance for the optimisation of the reaction condition in ion-exchange catalysis.

Future work on ion-exchange catalysis should aim to remedy the shortcomings of some of the researches of the current period. Firstly, the criteria for the choice of catalyst should be further refined, making allowance for the electrochemical properties of the active groups, the exchange capacity, the degree of cross-linking, the structure of the polymer network, the pore characteristics (for macroporous exchangers), and the thermal stability, using mathematical expressions for these properties. Secondly, our understanding of the role of indifferent solvents in ion-exchange catalysis must be extended in breadth and in depth, taking account of their influence on the distribution of reactants between the catalyst and the reaction medium. Thirdly, it is important to intensify the study of reaction kinetics and mechanisms, with special emphasis on the exact kinetic description of the properties of the catalysts. Fourthly, the thermal stability of the catalysts must be investigated, and means must be found to prevent ageing of the catalysts under practical conditions. Lastly, work on the synthesis of new ion exchangers with desirable thermal and mechanical properties must continue. Advances in all these directions will help to shorten the gap between the theoretical studies of the methods of ion-exchange catalysis and their general exploitation in the chemical industry.

While this article was in press, new papers have been published on the hydrolysis[231], hydration[232], dehydration[233-235], decomposition[236,237], esterification[238-243], ester interchange[244], alkylation[245-248], isomerisation[249], and condensation[250-252] of organic compounds in the presence of ion-exchange resins as catalysts. A special review of the dehydration of various compounds (mainly alcohols) has appeared[253]. The writer's thesis[254] presents a general discussion of ion-exchange catalysis.

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