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PRESENT STATE OF ION-EXCHANGE CATALYSIS

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1. CONCEPT OF ION-EXCHANGE CATALYSIS AND ITS TERMINOLOGY

Like the corresponding ions in homogeneous media, the counter-ions of the high-molecular-weight polyelectrolytes are capable of catalysing many organic reactions of varying character.

This new application of ion exchangers, which can be termed ion-exchange catalysis, is now being developed and our knowledge is still incomplete. Nevertheless, the results of both laboratory studies and industrial applications of ion exchangers as catalysts are encouraging for the future prospects of ion-exchange catalysis.

The catalytically active counter-ions of ion exchangers are in a solvated state, and in this respect are similar to the so-called free ions in ordinary electrolyte solutions. For that reason both the reactions catalysed in solution by ions and those catalysed by counter-ions of ion-exchange resins are able to proceed in accordance with the same mechanism, and are of the same kinetic order. The rate of a given reaction depends, however, on whether a given amount of catalytically active ions is present in the form of a soluble electrolyte, or in the form of an ion exchanger.

As suggested by Haskell and Hammett[1], the ratio of the reaction rate in a heterogeneous system to that in a homogeneous system, at equivalent concentrations of catalyst ions, is termed the efficiency of the ion exchanger. The efficiency of the ion exchanger q may be equal to, larger than, or smaller than unity, and depends on the properties of the catalyst itself, as well as on those of the solvent.

The essence of this concept may be exemplified by the irreversible first-order reaction of decomposition of AB into A and B, using Q_{AB} moles of the starting compound.

The rate of the reaction in a homogeneous system is $dQ_{AB}/dt = k_h.Q_{AB}$, where k_h is the velocity constant of a homogeneous reaction. For the corresponding heterogeneous reaction, carried out in the presence of an ion exchanger $dQ_{AB}/dt = k_{het}Q_{AB}$. The efficiency of the ion exchanger, *i.e.* the ratio between the velocity constants of the heterogeneous and homogeneous reaction is $q = k_{het}/k_h$. The relationship of the efficiencies of an ion exchanger for two compounds belonging to the same chemical class, is termed the specificity ratio[2]. If the reactants, *e.g.* esters, are simultaneously placed in contact with the catalyst, the value $r = q_1/q_2$ is a measure of the selectivity of the transformation of one component with respect to the other. This value is quantitatively related to the standard free energies of four intermediate states:

$$RT \ln q_1/q_2 = (F_{R_1} - F_{H_1}) - (F_{R_2} - F_{H_2}),$$

the subscript H corresponds to the reaction under homogeneous, and the subscript R to the same reaction under heterogeneous conditions of catalysis.

By changing the reaction conditions the efficiency of the ion exchanger with respect to different components in the mixture may be altered, and by changing the specificity ratio a more extensive conversion of one compound relative to another may be caused.

The efficiency of ion exchangers depends on the following factors: (*a*) the properties of the catalyst and the reactants, which determine the activation energy of the reaction; (*b*) the distribution constant of reactants between the solution and the catalyst; (*c*) the nature of the solvent.

The efficiency of ion exchangers may be less than unity if the distribution constant of the reactants between the resin and the liquid phase is less than unity. This includes the limiting case where, owing to their large molecular volume, the reactants diffuse slowly, or not at all, inside resin beads, so that the reaction is mainly limited to the interface.

The efficiency of ion exchangers is promoted by an increase in the distribution coefficient of the reactants and by changes in the system which cause a greater reduction of the entropy of formation of the active complex from the reacting molecules and the catalyst.

Riesz and Hammett[3] have shown that partial substitution of H^+ ions by quaternary ammonium cations results in an increased rate constant of the heterogeneous reaction of ester hydrolysis, in 1 N solutions. In all probability, the introduction into the resin of mobile ions similar to the reactant causes an increase in the distribution constant, and consequently, in the efficiency of the ion exchanger.

In certain cases the efficiency of the ion exchanger can be increased by introducing an organic solvent which would increase the solubility of the reactants. For example, the addition of ethanol considerably increases the rate of hydrolysis of fats in the presence of ion-exchange resins[4].

The addition of acetone has an adverse effect on the efficiency of sulphonated phenolformaldehyde cation exchangers in the saponification of acetates. In aqueous and aqueous acetone solutions containing $< 35\%$ acetone this resin is a more efficient catalyst than the equivalent amount of HCl. At high acetone concentrations the ratio of the velocity constants changes and the resin becomes a less efficient catalyst than HCl[5].

According to other authors[6,7] the efficiency of ion exchangers in the hydrolysis of a series of esters in aqueous solutions exceed unity, and increases with increasing molecular weight of the compound undergoing hydrolysis. If the same reaction is carried out in 70% aqueous acetone[8], the efficiency of the ion-exchange resin is less than unity, and decreases with increasing molecular weight of the compound hydrolysed.

The reaction rate in the above cases is affected by the distribution of the solvent between the ion exchanger and the liquid phase. The ion exchanger is undoubtedly enriched by the compound with the higher dielectric constant, namely water, while the concentration of acetone in the liquid phase rises. The ester concentration rises in the liquid phase enriched by organic solvent, and this is increasingly the case the longer their hydrophobic radical. This is why the rate of the heterogeneous reaction decreases with an increase in the ester molecular weight.

The rate of ion-exchange reactions is undoubtedly determined by the ratio of the reactant's molecular size to the size of "micropores" of the ion exchanger. It is therefore not surprising that the rate of sucrose inversion in the presence of a sulphonated phenolformaldehyde cation exchanger is smaller than in HCl solutions, and that it depends on the size of resin particles[9-11]. The efficiency of cation exchangers with compact structures as catalysts in the hydrolysis of esters is less than unity and decreases with increasing length of the molecule undergoing saponification. At a small degree of cross-linking the "micropores" of ion exchangers permit free passage of reacting molecules, and the process therefore proceeds faster under heterogeneous than under homogeneous conditions[12]. The efficiency of open-structure ion exchangers in the reaction of iodine with acetone also exceeds unity[13]. Finally, the rate of a reaction catalysed by ion exchangers depends on the concentration of the catalytically active counter-ions in the unit volume of catalyst.

This problem is considered in great detail, alongside the significance of diffusion in ion-exchange catalysis, in the work of Noller and Hässler[14,15] on the kinetics of the decomposition of aqueous diazoacetic ester into glycollic acid ester and elementary nitrogen. In this system six different specimens of sulphonic polystyrene cation exchangers were used as catalysts and their capacity for H^+ ions, varied by partial substitution with Na^+ ions, was 0.03, 0.31, 0.51, 1.06, 1.61, and 3.45 mg-equiv., respectively. The activity of the catalyst naturally depended on its content of H^+, since Na^+ ions do not accelerate the reaction.

Depending on the catalyst's activity, two limiting reaction mechansims are possible: (*a*) when the catalyst is not very active, and contains only a few protons in active sites per unit weight and the reaction molecules have to travel a long way inside the solid phase in order to react, the reaction proceeds slower than diffusion and therefore controls the kinetics; (*b*) when there are many protons per unit weight of the resin, the reaction proceeds faster than diffusion, and the cation exchanger's "pores" then contain the reaction products, the concentration of reacting molecules decreasing in the direction of the particle interior. Owing to the relatively small diffusion rate (which in this case governs the reaction kinetics) some of the cation-exchanger protons do not take part in its activity. For that reason, irrespective of the general increase of the reaction rate with increased concentration of H^+ ions, the velocity constant per 1 mg-equiv. of catalytically active ions must fall.

Experimental data show in fact that, for a constant quantity of ion exchanger (165 mg), the velocity constant of the decomposition of diazoacetic acid, referred to 1 mg-equiv. of catalytically active ions, increases as their concentration per unit weight of catalyst falls. Equal amounts of hydrogen ions accelerate the reaction in inverse proportion to their concentration per gramme of ion exchanger.

The general activity of sulphonic polystyrene cation exchangers in the decomposition of diazoacetic ester decreases with increasing concentration of H^+ ions in the catalyst, but the linear relationship between the velocity constant and the quantity of cation exchanger is not fulfilled. The above considerations emphasise the great effect of diffusion on the reaction rate of ion-exchange catalysis, which in this respect should be considered as a variant of the heterogeneous catalysis.

The experimentally established increase in the activation energy of diazoacetic ester[15] with increased concentration of H^+ ions in the catalyst, accords completely with the concept of diffusion as a factor governing the reaction kinetics. The actual activation energy, corrected for the energy of activation of diffusion, is independent of the amount of catalyst and practically equals its value for the reaction under homogeneous conditions. The identity of the intermediate compound in both cases becomes apparent here: irrespective of its phase composition, the catalyst (ion exchanger or a water-soluble acid) yields a proton to react with a molecule of the reactant and form a carbonium ion.

Further development of work on the reaction kinetics

underlying the ion-exchange catalysis is of great theoretical significance.

The important aim in the near future should be the construction of a general theory taking into account the effect of the various factors on the rate of reactions catalysed by ion exchangers. Such a theory should open new paths towards a systematic planning of chemical processes and establish favourable conditions for the further development and practical application of ion-exchange catalysis. Ion exchangers are already used in more than 20 types of different chemical reactions.

The extensive possibilities of the practical application of ion-exchange catalysis have aroused widespread interest in this new field of chemistry. Since 1946 an increasing number of publications have appeared dealing with ion-exchange catalysis, and since 1951 reviews have appeared in journals [16-23], ion-exchange symposia [24,25] and monographs [26,27] on the use of ion exchangers as catalysts in organic syntheses.

The present review, although not claiming to be exhaustive, covers the most important work on ion-exchange catalysis published prior to October 1961.

2 ION EXCHANGERS AS CATALYSTS IN HYDRATION

One of the most interesting and significant examples of the application of ion-exchange catalysis is perhaps the preparation of ethylene glycol by hydration of ethylene oxide.

The hydration of ethylene oxide is accelerated by all known sulphonic and phosphoric cation exchangers, and also, according to some data [28], by some strongly basic anion exchangers. According to some later results, however [29], neither the strongly basic anion exchanger AV-16† nor the medium basic anion exchanger EDE-10P‡ are efficient in catalysing the hydration of ethylene oxide. According to both the papers quoted above, the carboxyl cation exchanger, which is a polymerisation catalyst, does not accelerate this reaction, although other authors have indicated the possibility of hydrating ethylene oxide over the Amberlite IRC-50 resin [30]. The reaction rate in the presence of the carboxyl cation exchanger is one order of magnitude smaller than in the case of strongly acidic resin. Hydration can be carried out in a flask by stirring the mixture of ethylene oxide while adding large excesses of water and resin [31], or in a flow system [28,31] with an ion-exchange column as a reactor.

The scheme of one variant of the flow system is given in Fig. 1.

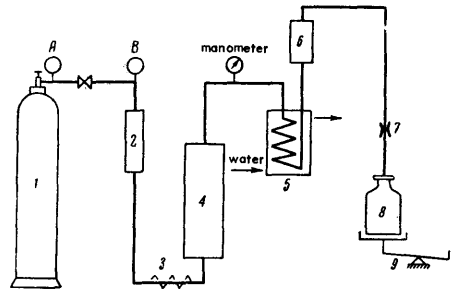


Fig. 1. Schematic diagram of the laboratory flow apparatus for ethylene oxide hydration.

About 20 litres of distilled water and the required quantity of ethylene oxide are introduced into the tank *2*. The reactor *4* is provided with a sieve (80 mesh), and packed with the sulphonic cation exchanger of type Amberlite IR-120. The reacting mixture is fed under pressure of nitrogen from cylinder *1* (nitrogen pressure is adjusted by regulator *B* and is indicated on pressure gauge *A*). The liquid flow is controlled by rotameter *6*, and the reactor temperature is determined by a thermocouple. The product is collected in receiver *8*, located on a balance.

One of the greatest advantages of the ion-exchange catalysis, the simplicity of the apparatus which is required, is quite obvious from this system.

This reaction shows another advantage of ion-exchange catalysts over soluble acids, namely greater selectivity. While the hydration to ethylene glycol in the presence of ion exchangers proceeds considerably faster than the side-reactions resulting in di- and tri-ethylene glycol, in the presence of sulphuric acid these transformations proceed at practically the same rate. As a result, under the conditions of homogeneous catalysis, the yield of side-products increases at the expense of that of ethylene glycol [29].

The indisputable advantages of the hydration of ethylene oxide over ion exchangers are: (*a*) the possibility of the continuous use of the catalyst, (*b*) the simplicity of its regeneration, and (*c*) the ease of separation of the product from the cation exchanger.

The only substantial disadvantage of the method of hydration described is the limited thermal stability of the ion exchanger. After a run of 5–6 h in a continuous plant at 50° the capacity of the cation exchanger KU-1§, and also KU-2¶, fell to 70–80%, and its sulphur content to 30–40%. In our view these losses can be reduced by removing the enormous heat of hydration of ethylene oxide with a special cooling system or by increasing the amount of water in the reaction mixture.

We have developed a method of hydration of tertiary pentenes, whereby the water used in the reaction is immobilised in the cation exchanger by preliminary swelling. Water is not introduced into the reactor as an independent liquid phase [32].

In its simplest terms, our method consists in placing tertiary pentenes, in contact with the hydrated KU-2 resin

† AV-16 is a polyfunctional, strongly basic anion-exchange resin prepared by the condensation of polyethylenepolyamines, pyridine, and epichlorohydrin. It contains secondary, tertiary, and quaternary (pyridinium) nitrogen groups (Ed. of Translation).

‡ EDE-10P is a polyfunctional weakly or strongly basic anion-exchange resin prepared by the condensation of polyethylenepolyamines with epichlorohydrin, and contains secondary, tertiary, and quaternary nitrogen groups (Ed. of Translation).

§ KU-1 is a difunctional, strongly acid cation-exchange resin with $-SO_3H$ and $-OH$ active groups, prepared by the condensation of *p*-phenolsulphonic acid with formaldehyde in acid (Ed. of Translation).

¶ KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

at room temperature, and subsequently decanting and fractionally distilling the catalysate [32]. The ion-exchange hydration of pentene differs from other methods of preparation of pentanol, *e.g.* the Grignard reaction or the hydrolysis of t-pentyl chloride, in being simple, economical, and safe [33].

Various sulphonic cation exchangers are suitable for the hydration of tertiary pentenes. The effect of different ion exchangers on the conversion of 2-methylbut-2-ene under non-equilibrium conditions is shown in Table 1. The main physicochemical properties of the resins are also given.

The data in Table 1 show that the catalytic activity of resins is determined not only by their exchange capacity, but by all their properties, which depend on the structure of the high-molecular-weight organic radical. The highest activity is displayed by the cation exchanger SBS, which is obtained by a two-stage sulphonation of rubber SKS-30†. The cation exchangers prepared by graft copolymerisation exhibit neither a high catalytic activity, nor a high exchange capacity, according to a recent report in the literature [34]. The cation exchanger SDV(VP), which exhibits very low exchange capacity with respect to sulpho-groups, is a very inefficient catalyst. The same holds for phosphoric acid cation exchangers of type KF-1‡ or VF.

As expected, the extent of the equilibrium conversion of tertiary pentenes to isopentyl alcohol is independent of the nature of the cation exchanger, but is inversely proportional to the concentration of hydrocarbons undergoing hydration in a mixture with other alkenes and alkanes.

The lower conversion of t-pentene due to dilution by inert solvents is incompatible with the classical laws of equilibrium.

The working hypothesis which accounts for the anomalous behaviour of this system is based on the assumption that the degree of association of isopentyl alcohol changes as a result of dilution with organic solvents. If it is supposed that at higher dilutions the degree of association of the t-pentyl alcohol is decreased, then the equilibrium of the reaction:

$$C_5H_{10}+H_2O \rightleftarrows C_5H_{11}OH\,,$$

should shift towards the left when the concentration of the hydration product is reduced. With a rise in concentration, the degree of association of the alcohol increases and the equilibrium is displaced towards the right.

The equilibrium of the system can be shifted in two ways, *i.e.* (1) by increasing the concentration of water in the system (or of its partial pressure in the case of the vapour-phase hydration), or (2) by removing the reaction product from the reaction zone. The use of the first method is limited in liquid-phase hydration by the small reciprocal solubility in the pentene–water system. For that reason the continuous removal of t-pentyl alcohol by excess water, or by another solvent immiscible with pentenes, leads to higher conversion.

The recent publication by Odioso and his coworkers [35] shows in fact that in a flow system, at 93.3°, in the presence of excess water, the conversion of the industrial pentane–pentene fraction over Amberlite IR-120 reaches 9.8%. In our view this method offers good prospects of being suitable for the selective extraction of tertiary pentenes, by whose dehydrogenation isoprene can be obtained simply and cheaply.

The hydration of pentenes and other alkenes proceeds according to a protonic mechanism *via* an intermediate formation of carbonium ions. Thus, the addition of the elements of water to isobutene in the presence of sulphonic cation exchanger ZSO_3H is preceded by the reaction:

$$(H_3C)_2C{=}CH_2+ZSO_3H \rightleftarrows (H_3C)_2C^+{-}CH_3+ZSO_3^-\,.$$

The carbonium ion formed in this way reacts vigorously with water to yield trimethylmethanol, while the catalyst is recovered:

$$(H_3C)_2C^+{-}CH_3+H_2O+ZSO_3^- \rightleftarrows (H_3C)_2COH{-}CH_3+ZSO_3H\,.$$

This reaction was recently carried out successfully over sulphonic cation exchangers by Menyailo *et al.* [36]. It has since been used as an industrial method for the preparation of trimethylmethanol, whose dehydration yields isobutene of high purity.

Attempts to hydrate propene over the weakly acidic cation exchanger KMG§ were unsuccessful, but this reaction proceeded very slowly over the phosphoric acid resin RF¶. [36] The strongly acidic cation exchangers were found to be very efficient catalysts of the hydration of propene [36]. Nonetheless, under the conditions employed (160°, 150 atm) these resins were not heat-resistant, and their activity rapidly deteriorated.

Like mercury salts, the Hg-form of sulphonic cation exchangers catalyses the addition of the elements of water to the acetylenic bond. In the presence of Hg-cation exchangers, acetylene [37], and phenylacetylene [38] form acetaldehyde and acetophenone, respectively.

TABLE 1. Effect of different cation exchangers on the conversion of 2-methylbut-2-ene at 50°.

Resin	Type of resin	Resin capacity for sulpho-groups, mg-equiv. per g		Coeff. of moisture capacity	Conversion of pentene, %	
		hydrated	anhydrous		1.5 h	4 h
SDV(VP)	vinylpyridine grafted on SDV-3 resin*	0.57	0.68	0.41	3.6	—
KU-2	sulphonated styrene – DVB copolymer	2.22	4.89	1.23	8.3	14.8
KU-1G	sulphonated phenol – formaldehyde resin	1.11	2.69	1.77	8.8	18.7
KU-1	ditto	1.14	2.13	0.83	10.3	19.5
SDV(VS)	vinylsulphonic acid grafted on the SDV-3 resin	2.24	4.05	0.93	10.9	19.7
SBS	sulphonated butadiene – styrene rubber	2.03	3.44	0.73	10.9	23.6

* SDV-3 is a strongly acidic cation–exchange resin with $-SO_3H$ groups. It is based on styrene (Ed. of Translation).

† Synthetic rubber made by polymerising butadiene + 30% styrene at 48°–50° (Ed. of Translation).

‡ KF-1 is a strongly acidic cation-exchange resin with $-PO_3H_2$ active groups. It is based on styrene, vinylnaphthalene, and acenaphthene (Ed. of Translation).

§ KMG is a weakly acidic cation-exchange resin with –COOH active groups (Ed. of Translation).

¶ RF is a strongly acidic cation-exchange resin with $-PO_3H_2$ active groups (Ed. of Translation).

3. ION EXCHANGERS AS CATALYSTS IN HYDROLYSIS

Inversion of sucrose in the presence of ion exchangers has an important place in investigations of this kind. One of the first studies[39] gave interesting results on the effect of the nature of the catalyst and of temperature on the inversion. These are collected in Table 2.

Table 2 shows that the rate of inversion increases sharply with a rise of temperature. A more detailed quantitative study of the kinetics of reaction carried out over sulphonated phenol–formaldehyde[40] or sulphonated benzaldehyde–phenol–formaldehyde cation exchangers[41] indicates a linear relationship between the logarithm of the velocity constant and the reciprocal of the absolute temperature. An increase in the amount of the catalyst, Amberlite IR-120 resin, also increases the velocity constant: according to Bodamer and Kunin[39] the 10^4k values at 50° and resin quantities of 5, 28, 40, and 80 g per 1 g sucrose are 4.8, 26.3, 34.4, and 71.6 min^{-1}, respectively. It follows from these results that the chemical reaction itself is the sole process controlling the rate of inversion of sucrose in the presence of cation exchangers.

The state of bonding of mobile hydrogen ions in active sites affects the catalytic activity of cation exchangers considerably. Thus, while all sulphonated cation exchangers with a limited degree of cross-linking are effective catalysts for inversion, the carboxylic resins either completely fail to accelerate this reaction[39,40], or, in the case of weakly cross-linked resins, fall far behind the strongly acidic cation exchangers in their activity. For this reason sulphonated cation exchangers are recommended for use in the industrial inversion of sucrose[42]. Processes such as the purification of sucrose, on the other hand, in which inversion is harmful, should be carried out in the presence of carboxylic cation exchangers[19].

Since the majority of reactions catalysed by ion exchangers are effected in the interior of the catalyst's beads, the reaction rate is greatly affected by the lattice structure, and above all, by the degree of cross-linking of the resin. The results in Table 3 show a linear relationship between minus the logarithm of the velocity constant and the degree of cross-linking of the cation exchanger. In the presence of the strongly cross-linked resin, at 50°, the inversion proceeds very slowly, while at room temperature it altogether stops. Consequently, the increased structural density of the resin, due to cross-linking, hinders internal diffusion, and may eventually lead to the localisation of the reaction at the surface of the ion-exchanger beads, or even to a complete standstill.

TABLE 2. Effect of the nature of the catalyst and temperature on the velocity constant of sucrose inversion.

Catalyst	10^4k at various temperatures		
	25°	50°	75°
Amberlite IRC-50	0.0	0.0	0.0
Amberlite IR-120	0.7	26.3	117.0
0.001 *N* HCl	—	0.5	12.0
0.18 *N* HCl	18.0	790.0	—

TABLE 3. Effect of the extent of cross-linking in Amberlite IR-120 resin on the velocity constant of sucrose inversion.

Divinylbenzene in the resin, %	10^4k at various temperatures		
	25°	50°	75°
1	7.6	199.2	—
10	0.7	26.3	117.0
20	—	0.7	23.2

Examples of the hydrolysis of other carbohydrates or esters show that the efficiency of ion-exchange catalysis is often determined by the size of their "micropores" and of the molecules undergoing transformation[43,44]. The data in Table 4 illustrate this conclusively.

It is obvious from Table 4 that ion-exchange catalysis offers great possibilities for the selective hydrolysis of the components of a mixture. Certain authors[43] indeed compare ion exchangers with enzymes in their capacity to catalyse reactions selectively.

If necessary, the ion exchanger can be activated for use as a catalyst of the hydrolysis of carbohydrates of large molecular weight[45]. Thus this can be achieved by the addition of acids which break down large molecules into smaller ones which can be transported into the beads of the ion exchanger. In most cases the total catalytic activity of the cation exchanger and the acid used simultaneously in the hydrolysis of starch exceeds the sum of the activities of the two components taken separately.

In certain reactions involving ion-exchange catalysis the specific interaction between the ion exchanger and the reactant improves the reaction kinetics. For example, owing to the capacity of proteins to form coordination bonds with the anions of the resin, Dowex-50 is a more efficient catalyst in their hydrolysis than are the water-soluble acids[46].

Sulphonated cation exchangers are used with advantage as catalysts in the hydrolysis of esters. The catalytic activity of the sulphonated phenol–formaldehyde cation exchanger Amberlite IR-100 is 11 times greater than that of a carboxylic cation exchanger of twice that capacity[6]. It is 1.8 times more active than the equivalent amount of HCl in the hydrolysis of methyl acetate, and this factor is increased to 2.3 in the hydrolysis of ethyl acetate, and to 20 in the hydrolysis of benzyl acetate. The very high

TABLE 4. The extent of hydrolysis of certain carbohydrates and esters[44].

Compound hydrolysed	Time, h	Temperature, °C	Extent of hydrolysis, %
Maltose	10	98	100
Glycogen	10	98	0
Ethyl acetate	10	65	100
Poly(vinyl acetate)	10	65	15.3
Methyl galacturonate	10	98	100
Poly(methyl galacturonate)	10	98	6.45

activity of cation exchangers can be explained by the positive sorption by the catalyst of molecules undergoing hydrolysis. The sorption increases with rising molecular weight of the ester. As mentioned above, the addition of large amounts of acetone lowers the efficiency of ion exchangers as catalysts for ester hydrolysis [1].

A thorough study of the kinetics of hydrolysis of a series of esters in 70% acetone was carried out by Haskell, Bernhard, and Hammett [1,8]. Their values for the velocity constant of hydrolysis in the presence of water-soluble acids (k_H) and the cation exchanger Amberlite IR-120 (k_R) are collected in Table 5.

As was expected, the rate of hydrolysis depends not only on the dimensions, but also on the structure of the ester molecule. The rate of hydrolysis of straight-chain esters decreases sharply with an increasing number of carbon atoms in the molecule. The effect of the chain length on the velocity constant is most pronounced in the case of an ion-exchange catalyst, since it also involves the slowing down of the internal diffusion. For that reason the efficiency of the ion exchanger q progressivley decreases from methyl acetate to ethyl n-octanoate. The increase of cross-linking in Amberlite IR-120 has the effect of further reducing the efficiency of the ion exchanger, which is more prominent in the hydrolysis of ethyl n-hexanoate than in that of methyl acetate. By changing the degree of cross-linking one can systematically alter the specificity ratio and thereby improve the selectivity of the hydrolysis of one of the components in a mixture of esters.

TABLE 5. Hydrolysis of esters in 70% acetone in the presence of 0.466 N HCl and Amberlite IR-120.

Ester	Temperature, °C	$10^6 k_H$, sec^{-1}	$10^6 k_H$, sec^{-1}	q	References
Methyl acetate	25.0	54.5	27.20	0.500	1
Ethyl acetate	25.0	46.4	15.00	0.330	1
Ethyl n-butyrate	25.0	19.2	2.56	0.134	1
Ethyl n-hexanoate	25.0	15.3	0.74	0.049	1
Methyl n-octanoate	25.0	16.8	0.95	0.056	8
Methyl phenylacetate	25.0	21.6	2.13	0.098	8
Methyl α-naphthylacetate	37.5	15.5	1.27	0.082	8
Methyl chloroacetate	25.0	38.0	11.00	0.29	8
Methyl benzoate	45.0	0.61	0.13	0.22	8
Methyl cyclopentanecarboxylate	25.0	24.0	3.47	0.14	8

The hydrolysis of esters can be carried out in plants of the continuous type, as described by Andreas [47] and Dierichs [48].

The hydrolysis of ethyl acetate solutions is catalysed by the addition of weakly or strongly alkaline ion exchangers, which are able to bind the acetic acid formed and thereby affect the reaction equilibrium [49]. It appears that the OH-form of Amberlite IRA-400 acts by the same mechanism. This resin was used for the hydrolysis of nicotinic nitrile into nicotinamide [50].

4. ION EXCHANGERS AS CATALYSTS IN ESTERIFICATION

Esterification is perhaps one of the main fields of the catalytic application of ion exchangers.

One important advantage of ion exchangers emerges from the study of esterification, namely the possibility of isolating compounds which cannot be isolated under the conditions of homogeneous acid hydrolysis. In this respect the esterification of polyhydroxyoxocarboxylic acids [51] and the preparation of the monoesters of lauric acid and diethylene glycol [52] are especially noteworthy. Homogeneous catalysis in the presence of acid yields only ethylene glycol diacetate with no more than trace amounts of monoester. Using sulphonated cation exchangers both mono- and di-esters are obtained, but the quantitative ratio of the reaction products depends on the reaction conditions. For instance, the reaction of equimolar amounts of lauric acid and diethylene glycol in the presence of toluene yields 24% monoester. By changing the ratio of acid to glycol to 1 : 4 and 1 : 6, and using sulphonated polystyrene resin as a catalyst, the yield is increased to 67 and 86%, respectively [52].

At an ethylene glycol : acetic acid ratio of 1 : 2, in the presence of 1% KU-2 resin the diester was obtained [29]. The efficiency of the ion exchanger in this synthesis is practically unity. The same resin sample showed no fall of activity when used nine times, but after that its activity decreased somewhat and disappeared almost completely after the eleventh run. It appears that in this case there is no irreversible resin change of the thermal desulphonation type [53,54], but rather a blocking of active sites by the large molecules of the reaction product, since the activity of the sample almost fully recovered after six days without use [29].

According to Losev and Trostyanskaya [55], who investigated the preparation of butyl butyrate, the sulphonated phenol–formaldehyde cation exchanger MSF† and the sulphonated styrene–butadiene copolymer (resin SBS) undergo an irreversible reduction of exchange capacity and catalytic activity during the esterification. Table 6 shows the change of the catalyst's acidity (which is a measure of the exchange capacity) after repeated use in the synthesis of butyl butyrate. As a result of the loss of catalyst's activity, the reaction time t increases with each run.

In view of their thermal instability, the authors [55] recommend that the resins should not be used as catalysts in esterification above 120°. Data in Table 6 show that the

TABLE 6. The change of activity of sulphonated cation exchangers during their repeated use as catalysts in esterification.

Resin	Initial acidity of resin (a), mg KOH per g resin	Run I		Run II		Run III		Run IV	
		t	a	t	a	t	a	t	a
SBS	140	60	124	203	100	300	90	320	87
MSF	174	37	101	44	77	71	64	—	—

† MSF is a strongly acidic cation with $-SO_3H$ and $-OH$ active groups. It is based on phenol (Ed. of Translation).

resin SBS is more heat-resistant than the cation exchanger MSF, although less catalytically active. The phosphoric acid cation exchanger FS is even less active, while the carboxylic resin KM‡ does not catalyse esterification at all.

Notwithstanding their low heat-resistance the sulphonated phenol–formaldehyde cation exchangers are widely used for the preparation of methyl and ethyl esters of chloroacetic, succinic, tartaric, maleic, and adipic acids[56], butyl esters of carboxylic acids[57], and diallyl phthalate[58], which is an important raw material in the manufacture of polyester resins. By replacing *p*-toluene sulphonic acid with a cation exchanger in the synthesis of diallyl phthalate the resinification of the reaction product can be avoided and its purification, which consists in the absorption of phthalic acid by an anion exchanger, can be greatly simplified. To increase the yield of the ester the reaction mixture C_6H_6 [58] or CCl_4 [56] is added to give an azeotropic system.

The esterification of n-butanol with oleic acid in the presence of a sulphonated phenol–formaldehyde cation exchanger[59] is characterised by a high velocity constant which is proportional to the catalyst surface per unit weight of the reacting mixture. It could be assumed that owing to large volume of the oleic acid molecule the esterification rate is governed by internal diffusion. An interesting feature of the reaction is the existence of a slow initial induction period, at the end of which the reaction proceeds according to second order kinetics.

The esterification of butanol with benzoic acid over Amberlite IR–120 and Dowex-50 is also characterised by an induction period. No induction period is observed when the cation exchanger has previously been treated with water or butanol[60].

Investigations of the kinetics of the vapour-phase esterification of acetic acid and butanol in the presence of KU-2 cation exchanger showed that the velocity constant of this reaction decreases with rising temperature. This unexpected fact, which is not observed in the liquid-phase reaction[61] is explained by the lower sorption of the reactants by the resin at higher temperatures.

Esterification in the liquid phase often proceeds at a lower rate in the presence of ion exchangers than under the conditions of homogeneous catalysis by acid solutions. Thus, after reaction of methanol and adipic acid for 3 h under various reaction conditions, the catalysate was found, under static conditions, to contain the following percentage of ester: without catalyst 48.5%, with cation exchanger 82.5%, and with H_2SO_4 91.9%. In the presence of the cation exchanger the reaction equilibrium is not established even after 3 h, while in the presence of sulphuric acid it is reached after 1 h.

To obtain esters on the preparative or industrial scale the esterification should preferably be carried out not under static conditions but by passing the reaction mixture through a column-type reactor.

Fig. 2 shows a simplified diagram of the column used in the preparation of methyl adipate[62]. Methanol–acid mixture is added to the top of the column packed with Wofatit resin, and heated by steam. A methanol vapour stream, introduced in the lower part of the column facilitates the elimination of water formed in the reaction through the top of the column. Owing to the shift towards equilibrium,

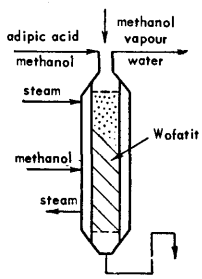


Fig. 2. Diagram of the column used for the preparation of methyl adipate.

pure ester is collected at the bottom. To secure continuous liquid flow, the column, 2 m long and 5 cm in diameter, has to be packed with cation exchanger (bead size 8–15 mm), obtained by cementing fine beads together with a Wofatit P gel[47]. At larger bead sizes of the cation exchanger the reaction proceeds slowly and yields a product containing large amounts of acid. Higher yield and purity of the end product can be achieved by using another column, packed by the finely ground ion exchanger, for preliminary esterification. The warm partly reacted mixture is then passed in through the top of the main column where the esterification proceeds to completion.

In an industrial plant producing 50 tons of ester monthly, the column for preliminary esterification is packed with 200 litres finely ground ion exchanger and the main column with 200 litres coarse resin.

The insufficient mechanical and thermal stability of cation exchangers tend to prevent the full utilisation of the plant. After two months' operation the mechanical losses of the resin are about 10%. Above 180° the thermal desulphonation of the cation exchanger and the loss of formaldehyde take place. In our opinion, under very harsh conditions both sulphonic polystyrene and sulphonic phenol–formaldehyde resins should be avoided.

In certain cases, as for instance in the synthesis of dibutyl phthalate, the cation exchanger partly dissolves in the reaction mass[63]. Such reactions should be carried out in the presence of soluble acids as catalysts.

When the thermal or chemical destruction of ion exchangers is excluded, the use of these catalysts in industrial esterification[47,57,64] can simplify the technology and lower the cost of production.

Esterification of carboxylic acids, like the hydration of alkenes, proceeds according to a protonic mechanism:

$$R'COOH+ZSO_3H \rightleftarrows R'C^+(OH)_2+ZSO_3^-,$$

$$R'C^+(OH)_2 \rightleftarrows R'C^+=O+H_2O,$$

$$R'C^+=O+ROH+ZSO_3^- \rightleftarrows R'COOR+ZSO_3H.$$

Besides the usual case of the reaction of carboxylic acids with alcohols, other reactions can also be used to obtain esters by ion-exchange catalysis. A few examples are considered below. Strongly acidic cation exchangers catalyse the liquid-phase esterification of alkenes by organic acids[18] with yields of the order of 50%. Esters derived

‡ KM is a weakly acidic cation-exchange resin with –COOH active groups (Ed. of Translation).

from diacetone alcohol can be prepared by reacting mesityl oxide[65] with alcohols in a column packed by the H-form of Dowex-50 resin.

Interesting liquid- and vapour-phase techniques have been suggested for the preparation of diethyl Cellosolve by reacting ethanol with ethylene oxide over sulphonic cation exchangers[66,67]. With KU-1 resin the consumption of ethylene oxide is considerably reduced as compared with the usual method of preparation under pressure. The yield of the principal product in the vapour-phase process is 95% at the start but is finally reduced to 80% owing to the formation of diethylene glycol monoethyl ether and the sorption of diethyl Cellosolve§ by the resin. Flushing of the cation exchanger by alcohol during the operation results in the removal of the sorbed diethyl Cellosolve and increases its yield.

Attempts to carry out the reaction at 140°–150° over KU-2 resin (which lowers the sorption of diethyl Cellosolve) were unsuccessful, since local overheating of the cation exchanger results in rapid charring and loss of activity[67].

In conclusion it may be added that the ion-exchange catalysis can be used to prepare esters by transesterification[15,68,69]. Interest in transesterification is continuously growing owing to the development of the chemistry of new synthetic materials. Transesterification of dimethyl terephthalate with ethylene glycol yields diethylol terephthalate, whose polymer is used in the manufacture of the of the best synthetic fibres — Lavsan. In industry the transesterification of dimethyl terephthalate is carried out in the presence of lithium oxide at 180°–200°, the reaction lasting 3–8 h. In the presence of the cation-exchange resin KU-2 this process, carried out at 140°–160°, is completed in 40–105 min with almost the quantitative yield of end-product[68].

Transesterification of methyl methacrylate with n-heptanol, n-octanol, or 2-ethylhexanol[68] is carried out at 130°–140°, and after 2–3 h gives the esters of these alcohols in 88, 32, and 89% yields, respectively. The lower yield of octyl methacrylate seems to be due to the larger size of both reacting molecules, which limits internal diffusion.

Transesterification can easily be carried out continuously. One such scheme is recommended for the transesterification of dimethyl adipate to dibutyl adipate. It should, however, be noted that under harsh reaction conditions (200°–210°) the life of the catalyst tends to be short.

5. ION EXCHANGERS AS CATALYSTS IN DEHYDRATION

As early as 1946 Sussman[4] demonstrated the possibility of dehydrating trimethylmethanol to isobutene using the sulphonated carbon Zeo-Karb H as a catalyst.

Quite resently Rozantsev *et al.*[33] carried out the dehydration of t-pentyl alcohol using the resin KU-2 in the hydrogen form.

In collaboration with the author of this review and Potudina, Markevich[70] made a thorough study of the kinetics of dehydration of t-pentyl alcohol over KU-2 resin and the phosphoric acid cation exchanger KF and found that the reaction product consisted of a mixture of tertiary pentenes, with 2-methylbut-2-ene predominating. The preparation of tertiary pentenes using ion-exchange resins differs from the standard method of dehydration by means of sulphuric acid in being simple, economical, and rapid. Another very important advantage of this method is the fact that the catalyst can be used several times without regeneration.

For selective dehydration of t-pentyl alcohol Odioso and his coworkers[35] used sulphonated polystyrene cation exchanger Amberlite IR-120. Heating a mixture of equimolar amounts of t-pentyl alcohol, pentan-1-ol, and pentan-2-ol to 200° yields a mixture containing 18.3% 2-methylbut-1-ene, 80.3% 2-methylbut-2-ene, 0.4% pent-1-ene, 0.3% *trans*-pent-2-ene, and 0.6% *cis*-4-pent-2-ene. Tertiary pentenes of sufficient purity are obtained from a mixture of pentanols by the same method.

Heated to 150°–170° in the presence of a sulphonic polystyrene resin, ethylene glycol undergoes dehydration to dioxan[25]. According to the author of a chapter on ion-exchange catalysis[25] the catalyst's activity remained unchanged in a continuous experiment lasting 40 h. Bearing in mind the limited heat-resistance of resins of sulphonated polystyrene type we doubt this statement and think that it requires further experimental confirmation.

The dehydration of another dihydric alcohol, butane-1,4-diol, resulting in the cyclic ether tetrahydrofuran, has been effected in the presence of cation exchangers[71]. Ethers are the main products of dehydration of primary aliphatic and aromatic alcohols, but they are usually somewhat contaminated with alkenes[72]. Yields of up to 80% are obtained.

Heating cyclohexanol to 145°–155° for 12 h in the presence of sulphonated phenolformaldehyde resin gave over 70% cyclohexene. Cyclohexane-1,2-diol undergoes dehydration at 185° forming a mixture of cyclohexa-1,3-diene and cyclohex-1-en-1-ol. Other cyclic alcohols behave similarly[73].

Terpenic alcohols also undergo dehydration in the presence of cation exchangers. According to Matsumoto[74], on distillation in the presence of the sulphonated phenolformaldehyde resin, terpinol hydrate yields terpineol. The author of this review and Kozlova found that under mild conditions (75°) the tertiary alcohol linaloöl undergoes dehydration in the presence of the hydrated H-form of the resin. Under the same conditions the primary alcohol geraniol withstands dehydration, but undergoes certain other chemical changes whose nature has not yet been definitely established. Investigations of the behaviour of terpenic alcohols in the presence of ion exchangers are very important for the chemistry of natural compounds. Work in this field should be further developed.

6. USE OF ION EXCHANGERS AS CATALYSTS IN ALKYLATION

Alkylation is in fact an addition of a paraffinic or aromatic compound to alkenes resulting in the formation of an alkane or an aromatic compound of higher molecular weight.

The application of ion exchangers as alkylation catalysts shows most promise in the alkylation of phenols, the reaction which is widely used for preparing the starting materials for the synthesis of surface-active agents, antioxidants, growth-promoting substances, weedkillers, perfumes, and many other valuable products[75–77].

§ Diethyl Cellosolve is ethylene glycol diethyl ether (Ed. of Translation).

According to current views the alkylation reaction proceeds *via* the formation of a carbonium ion[75] and is therefore accelerated by various acidic catalysts, including the strongly acidic sulphonic cation exchangers.

The replacement of liquid acid catalysts by solid ion exchangers was a big step forward in the technology of alkylphenols. The problem of the treatment of harmful phenol-containing waste waters was eliminated, the catalyst could be used repeatedly, and side-reactions were considerably reduced.

The school of Isagulyants[68,75,78-85] has carried out the most thorough and varied investigations of the application of ion exchangers to alkylation of phenols.

For better yields the cation exchangers used in alkylation should be free of water. Water is removed by heating *in vacuo* at 60°–90° to constant weight[79] or by boiling in benzene[82]. For heat-resistance, the sulphonated polystyrene resin KU-2 should be chosen in preference to the sulphonated phenol–formaldehyde cation exchanger KU-1, which is liable to undergo thermal desulphonation.

According to Isagulyants[79] the cation exchanger KU-2 gives good yields of alkylation products and can be used up to 12 times at 134°–135° without noticeable reduction of activity. Under the same conditions Vertlib and coworkers[82] used the cation exchanger KU-2 29 times, and then regenerated it by boiling with benzene and by subsequent treatment with 95% sulphuric acid for one hour. The static exchange capacity of the regenerated resin was, however, considerably lower (4.0 mg-equiv. g^{-1}) than that of the starting resin (5.4 mg-equiv. g^{-1}). It can be assumed that the lower exchange capacity is a result of the partial thermal desulphonation of the resin at the relatively high temperature required in alkylation. Alkylation can be effected under static conditions[79,82], in columns operating continuously[68,79], or by using the cation exchanger as a fluidised bed[85]. The general scheme of the most typical plants is given in Figs. 3–5.

The alkylating agents used are free alkenes (isobutene[68,84], diisobutene¶[68,79,86], isopentenes[68], cyclohexene[68], styrene[68], α-methylstyrene[68], octalin†, non-1-ene[86]), industrial mixtures of polymerised benzine type[79,82], and alcohols[78,79].

The alkylation of phenol by the diisobutene fraction boiling in the 95°–125° range gives a mixture of substituted phenols of molecular weight 200–210. Destructive alkylation, depolymerisation of diisobutene, and formation of substituted phenols of lower molecular weight, usually observed in systems using homogeneous acid catalysts, are absent in reactions catalysed by ion exchangers[79]. The absence of side-reactions is on the whole one of the greatest advantages of ion-exchange catalysis.

The most salient examples of the application of ion exchangers in alkylation reactions are collected in Table 7.

In most cases anhydrous resins had to be used, although the presence of moisture did not interfere with the course of the reaction[85].

Alkylation is carried out at 80°–165°, but cresols require milder conditions than phenols. The optimal amount of catalyst in the batch alkylation is 4–6.5% of the weight of reactants. Under dynamic conditions the yield of the final

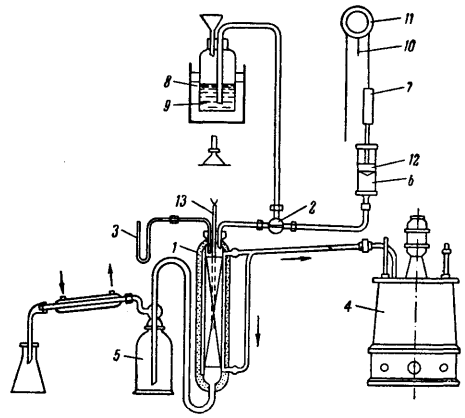


Fig. 3. Schematic diagram of the laboratory plant for the preparation of substituted phenols: 1) reactor; 2) three-way tap; 3) manometer; 4) thermostat; 5) receiver; 6) injection pump; 7) weight; 8) heating bath; 9) raw material container: 10) pendulum; 11) clock mechanism; 12) piston; 13) thermocouple.

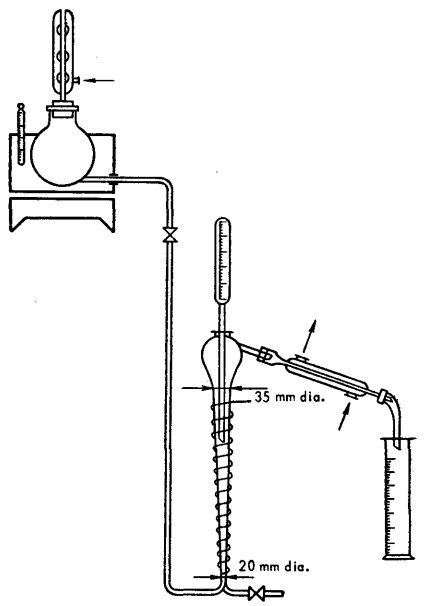


Fig. 4. Schematic diagram of the apparatus for the continuous alkylation of phenol in a fluidised bed of resin.

product is affected not only by the amount of catalyst and the temperature, but also by the rate of introduction of the reactants[79,85]. According to one of the most recent reports[85], for the alkylation of phenol by diisobutylene in a fluidised bed of KU-2 resin the reactants should be fed in at the rate of 3.5–4.4 ml per 1 g catalyst per hour. The reduction of the feeding rate to 0.5 ml only slightly increases the degree of conversion of phenol, while the increase to 5 ml per 1 g catalyst per hour interferes with the separation of the alkylate from the cation exchanger.

¶ 2,4,4-Trimethylpent-1-ene or 2,4,4-trimethylpent-2-ene (Ed. of Translation).

† Octahydronaphthalene (Ed. of Translation).

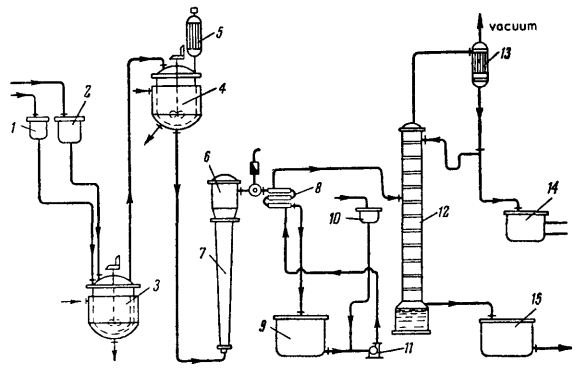


Fig. 5. Schematic diagram of an experimental plant for the continuous production of tertiary alkylphenol: 1) flowmeter for phenol; 2) flowmeter for isooctene; 3) mixing tank; 4) supply tank; 5) reflux condenser; 6) separator; 7) reacting column; 8) heat exchanger; 9) receiver for raw alkylphenol; 10) supply tank of alkali; 11) centrifugal pump; 12) fractionating column; 13) condenser; 14) florentine receiver; 15) receiver for dry alkylphenol.

TABLE 7. Most important uses of cation exchangers as catalysts in alkylation reactions.

Alkylating agent	Catalyst	Final product	References
Isobutene	KU-2 resin	t-butylphenol	68, 86
Diisobutene	KU-2 resin	t-octylphenol	68, 85
Polymer distillate	KU-2 resin	mixed alkylphenols	82
Cyclohexene	KU-2 resin	cyclohexylphenol	68
Styrene	KU-2 resin	methylbenzylphenol	68
α-Methylstyrene	KU-2 resin	dimethylbenzylphenol	68, 79
Octalin	KU-2 resin	α-decalylphenol	68, 79
Isobutyl alcohol	KU-2 resin	t-butylphenol	75, 78, 79
Isobutene	KU-1 and KU-2 resins	2,6-di-t-butyl-4-methylphenol	84
Isobutene	KU-2 resin	2-t-butyl-4-methylphenol	80
Isobutene	KU-1 resin	4,6-di-t-butyl-3-methylphenol	80
Pentenes	KU-1 and KU-2 resins	t-pentylphenol	83

It is noteworthy that the output of the plant operating with the fluidised bed of catalyst (Fig. 5) is 1.39 g alkylphenol per 1 ml reactant, which is 18 times higher than that obtained in plants with cyclic action when using the same catalyst, and 35 times higher than that obtained in the presence of benzene sulphonic acid. Moreover, alkylphenols obtained by ion-exchange catalysis form better quality detergents than the products of alkylation prepared in the presence of benzene sulphonic acid.

The industrial application of the catalytic alkylation of phenols over ion-exchange resins is still limited. This simple and highly productive method should be judged on its merits and given a proper place in industrial practice.

7. ION EXCHANGERS AS CATALYSTS IN POLYMERISATION

Only a little work has so far been devoted to the catalysis of polymerisation by ion exchangers.

From the accumulated data it is quite certain that cation exchangers can only catalyse the polymerisation reactions whose mechanism is protonic, and where there is no concomitant formation of high-molecular-weight molecules.

The sulphonic cation exchanger Wofatit F has been used as a catalyst in the polymerisation of acetaldehyde to paraldehyde[87,88]. The main practical difficulty in this process is the removal of the heat of reaction. An attempt was made to increase the surface of the Wofatit F by depositing it on porcelain Rashig rings or on pieces of copper wire. However, after heating the catalyst in acid and subsequently drying it, the cation exchanger did not remain on the carrier.

Satisfactory results were obtained by introducing a thin layer of the ion exchanger into the reactor by means of acetaldehyde fed from below and partly vaporised during the reaction. This principle forms the basis of a production plant with a daily output of 100 tons[87]. In case where high yields of the final products are obtained (99%) ion-exchange catalysis is greatly superior to the sulphuric acid method, and is more economical on energy (80%). There are no further references in the literature as to the industrial application of ion exchangers as catalysts in polymerisation reactions.

Papers by Odioso[35] and Menyailo and his coworkers[89] contain occasional items of information about the activity of cation exchangers as catalysts in the polymerisation of alkenes. In collaboration with Tulupov, Federov, and Tsekhmister, the author of this review has made a special study[90] of the polymerisation tertiary pentenes and isobutylene in the presence of the KU-2 cation exchanger. According to the authors[90], heating a mixture of 85% 2-methylbut-2-ene and 15% 2-methylbut-1-ene with the anhydrous KU-2 resin at 100° for 2, 24, 107, and 346 h yields 28, 67, 70, and 90% polymer, respectively, calculated on the pentenes introduced. At 150° the conversion of pentenes in 2 h is increased to 45%, but the resin deteriorates considerably due to thermal desulphonation. At the same temperature, but in isopentane solution, the cation exchanger KU-2 is more heat-resistant.

Heating the industrial butane–butene fraction in the presence of the hydrated form of KU-2 resin to 50° results in the selective hydration of isobutene yielding trimethylmethanol. Normal butenes do not react. At 75°, and even more at 100°, polymerisation starts to compete with hydration. The character of reactions catalysed by ion exchangers therefore depends not only on the properties and the physical state of the catalyst, but also on the temperature.

The anhydrous KU-2 cation exchanger catalyses only the polymerisation reaction, which involves isobutene and, to a lesser extent, normal butenes. Polymerisation in the presence of the KU-2 cation exchanger can thus be used for the selective removal of isobutene and the purification of the butane–butene fraction. If a method were found of increasing the selectivity of polymerisation of isobutene, cation-exchange catalysis could be used industrially for pretreating the butane–butene fraction as a raw material for the production of butadiene.

Our own results show that the sulphonic polystyrene cation exchanger catalyses the polymerisation of diene hydrocarbons[91]. The polymerisation of isoprene over an anhydrous cation exchanger proceeds very slowly, and a viscous product of molecular weight 785 is formed.

In the presence of the H-form of KU-2 resin in the state of maximum swelling the chemical transformations of isoprene are much more rapid and complex. In this case,

hydration accompanies polymerisation. Cyclopenta-1,3--diene undergoes similar changes, but less rapidly.

The discovery of the catalytic transformations of isoprene on cation exchangers has considerable relevance to the problem of the mechanism of formation of terpenes and their derivatives during plant metabolism. In this field ion-exchange catalysis has a point of contact with the chemistry of natural products.

8. ION EXCHANGERS AS CATALYSTS IN CONDENSATION REACTIONS

There is an abundant bibliography concerning the application of ion, especially anion, exchangers as catalysts in condensation reactions. The most typical reactions carried out in the presence of ion exchangers are considered below.

(a) Aldol condensation and crotonisation. The condensation of carbonyl compounds occurring as the result of the addition of an hydrogen atom from a methyl or α-methylene group of one molecule to a carbonyl oxygen of another molecule has been termed the aldol condensation:

$$RCH_2CHO + R'CH_2CHO \rightarrow RCH_2CH(OH)CHR'CHO.$$

Under the conditions which favour dehydration of the resulting aldol, unsaturated compounds of crotonaldehyde type are obtained:

$$RCH_2CH(OH)CHR'CHO \rightarrow H_2O + RCH_2CH = CRCHO.$$

This has been termed crotonisation.

In homogeneous media both types of reaction proceed side by side and are accelerated by many acidic and alkaline catalysts, including amines[92]. They are also catalysed by cation and anion exchangers.

Air-dried[93] or anhydrous[94] resins are used as catalysts. Owing to their low thermal stability the strongly basic anion exchangers should be dehydrated *in vacuo*. Precautions should be taken against the inactivation of strongly basic anion exchangers by carbon dioxide from air (owing to conversion of the hydroxyl form into the carbonate form) or by carboxylic acids, which react with the resins according to the scheme[94]:

$$R_4NOH + R'COOH \rightarrow R_4NOCOR' + H_2O.$$

The following techniques are used in the condensation of carbonyl compounds: (*a*) mixing reactants with the resins, followed by the distillation of the unreacted carbonyl compound and (sometimes) subsequent dehydration of the aldol; (*b*) heating the catalyst and the reactant with benzene (in order to remove water in an azeotrope) in an apparatus fitted with reflux condenser and water separator until no more water separates (this method is convenient for aldehydes which undergo condensation with difficulty); (*c*) filtration through a column packed with freshly regenerated resin[93] (used with easily condensed carbonyl compounds).

The aldol condensation may arise between two molecules of the same aldehyde, and between two different aldehydes, as well as ketones. The course and the yield of the reaction depend not only on the nature of the reactants and the catalyst, but also on the temperature and the presence of an inert diluent. In this connection mention should be made of the work of Durr[95], who studied the condensation of acetic and other aldehydes in the presence of various ion exchangers.

The condensation of acetaldehyde in a metal bomb at 130° proceeded vigorously only in the presence of the hydroxyl--form of the weakly basic anion exchanger Amberlite IR-4B. The distillation of the catalysate, obtained from 200 g acetaldehyde in the presence of 10 g anion exchanger gave 32 g acetaldol, 20 g crotonaldehyde and considerable amounts of a resinous residue. At 70° the same catalysate contained 45 g aldol and 12 g crotonaldehyde, since the conditions were less favourable for dehydration. Only a small amount of crotonaldehyde was formed when the strongly basic anion exchanger Amberlite IRA-400 was used, while the strongly acidic cation exchanger Amberlite IR-120 caused the formation of resinous products.

In the cold and in the presence of a sulphonic cation exchanger acetaldehyde undergoes polymerisation, forming 56% paraldehyde in a week. At the same temperature, but in the presence of a strongly basic anion exchanger, methylacrolein and acetaldol are formed in 18.6 and 8% yields, respectively. In the presence of a weakly basic anion exchanger the yields of these products are 8.8 and 19%, respectively. Thus, the strongly basic anion exchangers favour crotonisation, and the weakly basic ones favour aldolisation. The strongly acidic cation exchanger induces the formation of the cyclic paraldehyde[95].

Ueno[96] carried out the aldol condensation of acetaldehyde in ether solution at -2°, using a strongly basic anion exchanger in OH- or CN-forms. Ch'êng Ts'u-hing and his coworkers[97] studied the kinetics of the aldol condensation of acetaldehyde in 10–30% aqueous solutions and showed that the reaction is of the first order, and that the strongly basic anion exchangers are more active as catalysts than those which are weakly basic. According to Ueno and Yamagishi[98] higher yields of aldol are obtained over the CN- than over the OH-form of the strongly basic anion exchangers.

An interesting example of the combined use of a cation and an anion exchanger in the preparation of acetaldol and crotonaldehyde has been described by Mastagli[99]. This author started from paraldehyde, which on heating with a sulphonic cation exchanger was depolymerised to acetaldehyde, which underwent condensation to aldol and crotonaldehyde under the influence of the strongly basic anion exchanger which was also present. The very important conclusion drawn from this work was the independent catalytic action of cation and anion exchangers when present together.

According to Austerweil and Pallaud[100] the aldehydes of relatively low molecular weight are most susceptible to aldol condensation on ion exchangers.

The condensation of butyraldehyde results in the formation of the aldol intermediate, which readily undergoes dehydration to form α-ethyl-β-propylacrolein. According to Durr[101], butyraldehyde does not form the aldol in the presence of the OH-form of a strongly basic anion exchanger. When cold butyraldehyde is passed through a column packed with a strongly basic anion exchanger much heat is released, and the emerging liquid begins to boil. The catalysate obtained from 100 g butyraldehyde contained 38 g α-ethyl-β-propylacrolein and resinous products, but no trace of the aldol[95]. Under static conditions and in the presence of the same anion exchanger a viscous liquid was isolated after three days. It presumably consisted of a butyraldehyde trimer[95]. The weakly basic anion exchanger Amberlite IR-4B is less active under these conditions and forms a large amount of aldol, while the sulphonic cation

exchanger Amberlite IR-120 is inactive in the cold under both static and dynamic conditions. After 3 h at 75°, 10 g Amberlite IR-120 and 200 g butyraldehyde yield 88 g α-ethyl-β-propylacrolein. Amberlite IR-4B and particularly Amberlite IRA-400 are less effective under these conditions, giving 35 and 12 g α-ethyl-β-propylacrolein, respectively [95].

Astle and Zaslovsky [93] made a complete analysis of the catalysate obtained by passing butyraldehyde through a column 60 cm long and 4 cm in diameter. Their results are collected in Table 8 .

As shown in Table 8, the composition of the catalysate depends on the reaction time and on the nature of the catalyst. The formation of aldol alone in the presence of the strongly basic anion exchanger Permutit S is somewhat unexpected. Its dehydration does not occur even in the presence of Zeo-Karb. The conversion of De-Acidite from the hydroxyl- into the acetate-form gives increased activity for the crotonisation. The increase of the catalytic activity of weakly basic anion exchangers sometimes observed in the course of the reaction can be explained as the replacement of the hydroxyl ions in the catalyst by carboxylate ions which are always present in small amounts in aldehydes [93]. It appears that this also explains the increase in yield with increasing contact time.

The majority of authors prefer the weakly basic anion exchangers as catalysts in the condensation of aldehydes. The strongly basic anion exchangers rapidly become inactive [92] and require frequent regeneration even when operating at moderate temperatures.

Although more stable, even the weakly basic anion exchangers lose some of their activity after repeated use.

The decline in the activity of Amberlite IR-4B during the condensation of heptanol is caused by the sorption of the reaction products, blocking the bead surface. The activity of the resin can be maintained in such cases by freeing it from the reaction products by washing it after every run with toluene, benzene, petroleum ether, or some other inert solvent.

The condensation of heptanol over ion exchangers yields heptylideneheptanal [95]. At room temperature this reaction can only be effected by passage through columns packed by Amberlite IRA-400. Amberlite IR-4B is less effective in catalysing this reaction, while the sulphonated cation exchanger Amberlite IR-120 is inactive.

Under static conditions the reaction starts at 90° with Amberlite IR-4B, and at 120°–125° with Amberlite IR-120. At 125° the strongly basic Amberlite IRA-400 is completely devoid of catalytic activity, probably owing to its limited heat-resistance. By raising the temperature from 110° to 125° the yield of heptylideneheptanal in the presence of Amberlite IR-4B rises from 23.9 to 34.8%, but remains unaffected by further temperature increase. The attainment of the limiting yield can be more readily accounted for by the catalyst inactivation and partial solution, than by the reversibility of the reaction, for in the presence of Amberlite IR-120 and at 150°–155° the conversion of heptanal reaches 48.9% after the usual reacting time of 1 h. By increasing the contact time, the yield of the reaction product can be increased, but in no case is the conversion quantitative. The yield of the end product is also affected by the amount of catalyst present. For instance, at the optimal reaction temperature (145°) and after 2 h, the yields of heptylideneheptanal obtained in the presence of 1, 8, and 15 g Amberlite IR-120 per 100 g heptanal were 31.6, 67.4, and 73.9%, respectively.

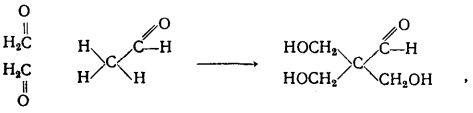
TABLE 8. Effect of the nature of anion exchanger and the contact time on the composition of products in the condensation of butyraldehyde.

Catalyst	Reacting time, h	Weight of catalyst per 100 g butyraldehyde	Yield, %	
			aldol	α-ethyl-β-propylacrolein
De-Acidite acetate	5	35	22	50
De-Acidite acetate	25	30	17	70
De-Acidite acetate	11	20	26	27
De-Acidite	48	30	53	3
Permutit S	20	30	66	0
Amberlite IR-4B	20	30	0	50

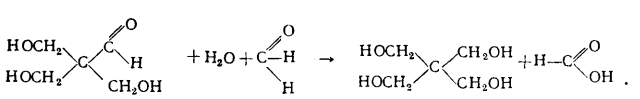
Astle and Pinns made a thorough study of the catalytic properties of sulphonic cation exchangers towards various other aldehydes [102]. They used Dowex-50 and Amberlite IR-120, which after the usual purification they dried in the air, and then *in vacuo* at 60°–65°. These authors disputed the above data of Durr [95] and showed that even at room temperature in the presence of sulphonic cation exchangers various aldehydes, including butyraldehyde, undergo polymerisation to form cyclic trimers and small amounts of dialkylacroleins. At higher temperatures the conditions become more favourable for dehydration, and the yield of dialkylacroleins rises. Dilution of aldehydes, particularly butyraldehyde, by inert solvents such as benzene, lowers the conversion into dialkylacrolein. The addition of water to the mixture of reactant and catalyst has the same effect. For this reason the decline of the resin's activity on repeated use may also be due to the absorption of water, and not solely to thermal decomposition.

Prolonged refluxing of the reaction mixture may reduce the yield of dialkylacroleins although the total conversion remains constant. In such cases the reaction product was found to contain higher amounts of compounds with –C–O–C–O–C– chains, and non-conjugated carbonyl groups [102]. It appears that, in the presence of cation exchangers the aldehydes may form not only cyclic trimers and dialkylacroleins, but also complex products of rather high molecular weight. So far the discussion has covered only the condensation of identical aldehydes, and a brief account of the condensation of two different aldehydes is given below.

The greatest promise is shown by the condensation of formaldehyde and acetaldehyde. The aldolisation of two molecules of formaldehyde and one molecule of acetaldehyde yields a complex aldehyde:



which subsequently undergoes the Cannizzaro reaction with another molecule of formaldehyde, forming pentaerythritol:



The synthesis of pentaerythritol in the presence of the OH-form of a strongly basic anion exchanger has been described in the patent literature [103]. It can, however, be assumed that under stated reaction conditions the catalysts are in fact OH^- ions, driven out into the liquid phase by chloride ions, introduced in the form of NaCl, while the role of the anion exchanger is to bind the formic acid produced in the Cannizzaro reaction. We attach importance to the application of ion-exchange catalysis in the condensation of formaldehyde and acetaldehyde to form acrolein, especially after the recent discovery of a cheap method for the manufacture of acetaldehyde by direct oxidation of ethylene [104].

The condensation of two different aldehydes was investigated by Durr [95,105] and Mastagli [99,106]. Mastagli and his coworkers showed that α-furfurylidenehexanal can be obtained in high yield by the condensation of furfural with hexanal at 118°–120° in the presence of Amberlite IRA-400. Under conditions of homogeneous alkaline catalysis this reaction yields large amounts of by-products. The same catalyst was used in the condensation of furfural with acetone to form monofurfurylidenacetone and small amounts of difurfurylideneacetone [106].

The aldol condensation and crotonisation can also take place between ketones. The weakly basic anion exchangers of types Amberlite IR-4B and IR-45 are, however, incapable of catalysing the condensation of acetone. Only in the presence of a strongly basic anion exchanger is acetone converted into diacetone alcohol [93,107]. The resulting aldol can be dehydrated with high yields to form mesityl oxide if the still of a Soxhlet apparatus is filled with acetone and the sulphonated cation exchanger Zeo-Karb, and the extractor is packed with Amberlite IRA-400. In view of the current availability and low cost of acetone, the practical application of ion-exchange catalysts in the preparation of a very valuable product such as mesityl oxide becomes a possibility.

(b) The Knoevenagel and Pechmann condensations. In its simplest form the Knoevenagel reaction is the condensation of a carbonyl compound with compounds whose methylenic hydrogen atom can easily be substituted by the radicals corresponding to aldehydes and ketones:

$$RR'CO + CH_3COCH_2COOC_2H_5 \rightarrow CH_3COC(=CRR')COOC_2H_5 + H_2O.$$

The Knoevenagel reaction is catalysed by liquid amines and anion exchangers. It is usually effected by heating to 90°–100° the mixture of an aldehyde or ketone and acetoacetic or similar esters with 10% by weight of the resin. After refluxing for 2 h the resin is separated on a Buchner funnel, and the reaction products extracted by ether. In certain cases a cation exchanger is added to the anion-exchanger catalyst [108].

The composition of the product formed in the presence of mixed anion and cation exchangers depends on the ratio of the catalyst's components. Such procedure can yield not only open-chain compounds, but also cyclic derivatives.

In certain cases the role of the cation exchanger is to accelerate the reaction which yields the starting compounds required in the Knoevenagel condensation.

Thus, Mastagli and Lagrange [109] used a cation exchanger as a catalyst of the saponification of heptanacetal and the OH-form of an anion exchanger for the subsequent condensation of the resulting heptanal with ethyl ester of cyanoacetic acid.

In the condensation of isobutyraldehyde and butyraldehyde with ethyl acetoacetate it was shown that [93] the weakly basic anion exchangers (Amberlite IR-4B, De-Acidite in the OH- or CH_3COO-form) are more efficient catalysts of the Knoevenagel reaction than the strongly basic anion exchangers Amberlite IRA-400 and Dowex-1. It is possible, however, that the lower activity of the strongly basic anion exchangers is due to their inactivation by standing in the air or in the presence of acid, *e.g.* CH_3COOH.

Trivedi [110,111] successfully applied the strongly basic anion exchangers, *e.g.* Amberlite IRA-400 to the synthesis of coumarin and 3-cyano-4,6-dimethyl-2-pyridone.

Mastagli and Andric [112] described a method for synthesising 3-acetylcoumarin by reacting salicylaldehyde with ethyl acetate in the presence of anion exchangers. In the cold this reaction took one month. At 75°–85° it lasts 3 h, but the yield of the product is considerably smaller.

Another method for obtaining coumarin derivatives consists in reacting β-ketoesters [112,113] or malic acid with phenols. This is the so-called Pechmann condensation, in which Amberlite IR-120 can be used instead of sulphuric acid. The higest yields of coumarin derivatives are obtained if the reaction is carried out in hexane solution, in which the β-ketoesters are strongly enolised.

(c) Condensation of aldehydes and ketones with alcohols. The condensation of aldehydes with alcohols to form acetals is catalysed by the H-form of cation exchangers. The catalytic efficiency of the cation exchanger depends on its heat-resistance, on the strength of its active groups, and on their position in the resin macromolecule [114].

Acetals are prepared by heating the reactants at 110°–120° in the presence of a sulphonated cation exchanger until no more water separates. The acetal derived from furfural and n-heptanol was obtained in this way [115], and so were the acetals derived from benzaldehyde and butanol, hexanol, or heptanol [116].

The interesting work by Astle and his coworkers [117] deals with a continuous method for the preparation of acetals and ketals from ethylene glycol. Aldehydes react more readily than ketones. The conversion of the aldehyde studied was 60–100%.

The reaction of paraformaldehyde with diethylene glycol in the presence of a sulphonic cation exchanger gave a cyclic acetal, capable of forming wax-like polymers [117].

(d) Certain specific condensations. Strongly basic anion exchangers in the CN-form effectively catalyse the benzoin condensation [94,118]. Benzaldehyde (50 g), ethanol (100 g) and water (40 g) are refluxed for 2 h in the presence of the CN-form of Amberlite IRA-400 (75 ml). The reaction mixture is filtered while still hot, and 39 g benzoin separates on cooling the filtrate (79% yield). This method can also be applied to preparing furoin from furfural and *p*-dimethylaminobenzoin from *p*-dimethylaminobenzaldehyde and benzaldehyde [94].

Anion exchangers have also been used as catalysts in the condensation of aldehydes and nitroalkanes to form nitroalcohols [94,119,120].

Schmidle and Mansfield [94] described the preparation of 1-nitrobutan-2-ol by passage of 58 g propionaldehyde, 91 g nitromethane, and 50 g ethanol through a column packed

with the OH-form of Amberlite IRA-400 at 27° – 30°. The product was obtained by distillation of the filtrate. This simple method gives fairly high yields (up to 70%) and can be used for the synthesis of 2-nitropentan-3-ol, 2-nitrohexan-3-ol, and 1-nitropentan-2-ol. The synthesis of 2-nitroethanol from nitromethane and formaldehyde, however, proceeds with difficulty and the yield is small (up to 9%) [119]. The weakly basic anion exchangers do not catalyse the condensation of nitromethane with formaldehyde and other aldehydes. Nonetheless, the condensation of 2-nitropropane with various aldehydes is more efficiently catalysed by the weakly basic anion exchanger Amberlite IR-4B than by strongly basic resins. The catalytic activity of an anion exchanger is therefore determined not only by its basicity and the type of reaction catalysed, but also by its own steric properties and those of the reactants.

Certain reactions, for example, the condensation of acetone and cyclohexane with nitromethane or nitroethane, have been carried out in the presence of strongly basic anion exchangers with satisfactory yields, but the reactions took several days.

Finally, mention may be made of two more condensation reactions, still in the experimental stage. In one of them, namely the condensation of formaldehyde to form lower sugars [121], an anion exchanger saturated with α-aminoacetophenone was used as catalyst. It should, however, be noted that in this case the anion exchanger was only the carrier of the catalytically active compound, which was bound to it by the van der Waals forces.

The other reaction is of interest as a possible method for the selective extraction of isopentenes from the pentane–pentene cracking fraction. The condensation of tertiary pentenes with paraformaldehyde is catalysed by cation exchangers [79], while in the presence of water-soluble acids it is not so well defined. Isagulyants [79] succeeded in obtaining good yields of isohexyl acetate by condensation of 2-methylbut-2-ene with paraformaldehyde in acetic anhydride solution and in the presence of a cation exchanger. It may be of interest to undertake a detailed study of the Prins reaction using other hydrocarbons, particularly isobutene.

9. ION EXCHANGERS AS CATALYSTS IN CERTAIN OTHER REACTIONS

The above examples demonstrate sufficiently clearly the essential principles underlying ion-exchange catalysis, its merits, and its shortcomings, although they do not exhaust all the possibilities of its practical application. In Table 9 are listed briefly some reactions of addition, cyclisation, structural rearrangement, etc., which can be carried out in the presence of ion exchangers.

It should especially be emphasised that inorganic ion exchangers are beginning to be used as catalysts of organic reactions. Their great chemical and thermal stability [150] distinguishes them favourably from their organic counterparts. Chemists should take notice of these new ion exchangers and do their best to develop methods for their use as catalysts in reactions requiring high temperatures.

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The catalytic action of ion-exchange resins is based on the capacity of mobile ions in their active sites to participate in the formation of unstable intermediate compounds with the molecules of one of the reactants.

Reactions in which the intermediate product is a carbonium-type cation are catalysed by cation exchangers. The anion-exchanging resins catalyse the reactions characterised by the intermediate formation of anionic complexes.

In rare cases, such as the aldol condensation, both cation and anion exchangers are active. Probably, both cationic and anionic complexes can be formed in such reactions.

If in a multistage process one stage yields a cationic complex, and another an anionic complex, a mixed catalyst should be used, consisting of both a cation and an anion exchanger. When both are present, the component reactions proceed independently.

TABLE 9*. Some further examples of the application of ion exchangers as catalysts.

Type of reaction	End product	Type of catalyst	References
Cyclisation	tetrahydropyrans	sulphonic cation exchangers	122
Cyclisation	2,3-dimethylindole	strongly basic anion exchanger	123
Michael reaction	nitro-derivatives	strongly basic anion exchangers	124
Protein hydrolysis	amino-acids	sulphonic cation exchangers	125
Rearrangement	unsaturated ketones	sulphonic cation exchangers	38
Addition	cyanohydrins	strongly basic anion exchangers	94
Addition	4-methoxy-4-methyl-2-pentanone	sulphonic cation exchanger	65
Addition	bis-(2-cyanoethyl) ether	strongly basic anion exchanger	94, 109, 126, 127
Addition	epoxides	inorganic ion exchangers	128
Addition	epoxides	cation exchangers	129
Decomposition	phenol and acetone	sulphonic cation exchangers	130, 131, 132
Decarboxylation and saponification	esters, alcohol, acids	sulphonic cation exchangers	133
Saponification	alcohols and acids	sulphonic and carboxylic cation exchangers	134
Saponification	alcohols and esters	sulphonic cation exchangers	135
Esterification	ethyl glucuronate	anion exchanger	136
Dehydration	isobutene	sulphonic cation exchanger	137
Oxidation	glutaric acids	sulphonic cation exchangers	138
Oxidation and esterification	esters of ω-acyloxyalkyl-ω-hydroxyalkyl carboxylic acids	sulphonic cation exchangers	139
Nitration	various nitro-derivatives	sulphonic cation exchangers	140
Ring-opening	1,3-diols	sulphonic cation exchangers	141
Alkylation	alkylation products of ethers and phenols	sulphonic cation exchangers	142
Alkylation	*p*-t-butylphenol	sulphonic cation exchanger	143
Condensation	mesityl oxide	sulphonic cation exchanger	144
Exchange of functions	acetals, unsaturated ethers	sulphonic cation exchangers	145
Polymerisation	polymers of dienes	sulphonic cation exchangers	146
Polymerisation	isobutene polymers	sulphonic cation exchangers	147
Hydration	t-pentyl alcohol	sulphonic cation exchanger	148
Condensation	4,4-dihydroxydiphenylethane	sulphonic cation exchanger in Hg-form	149
Condensation	α-Furylnitroethylene	anion exchanger	151

* This table contains certain data published after the present review was written, and certain reactions not covered by Sections 2–8.

The majority of reactions catalysed by ion exchangers proceed in the ion-exchanger pores, since the reactants and the reaction products diffuse in opposite directions. The velocity of a reaction catalysed by ion exchangers therefore depends on the ratio of the reactant's molecular size and the size of the catalyst's "micropores", and consequently on the structure of the catalyst's lattice. In the selection of the catalyst therefore attention should be paid to the degree of cross-linking in an ion exchanger. Organic reactions involving large molecules should be carried out on ion exchangers with open structures. The important factors in the catalytic activity are also the bead size, swelling, exchange capacity, and the state of bonding of the mobile ion in active sites. In the majority of cases the ion exchangers which are strong electrolytes are more effective as catalysts than the weakly acidic cation exchangers or the weakly basic anion exchangers. The exceptions to this rule can be accounted for by the chemical changes of the catalyst itself giving rise to secondary reactions.

The velocity of a reaction catalysed by ion exchangers is greatly affected by the nature of the solvent. The addition of compounds which have the effect of concentrating the reacting molecules within the ion-exchanger bead increases the rate of conversion.

Slow reactions are usually carried out under static conditions, by agitating the catalyst with the reactants in some sort of reactor, or by refluxing their mixture. The rapid reactions are carried out in the flow of reactants, and the catalyst is fixed either in a Soxhlet extractor, or in a column.

The simplicity of the apparatus for the continuous process, and the ease of the separation of the products from the catalyst are certainly the greatest merits of ion-exchange catalysis. Other advantages are the repeated use of the catalyst, and the ease of its regeneration. Another advantage still is the absence of side-reactions. Reaction products are obtained in high yields and do not require additional purification. Ion exchangers can therefore be used for the processing or the preparation of compounds which are unstable under the conditions of homogeneous catalysis with acids or alkalis. Moreover, the reactions catalysed by ion exchangers are selective, and a fact very important in industry, they simplify the treatment of waste waters compared with that when acid or alkaline liquids are used.

All this has stimulated the development of ion-exchange catalysis into an independent and promising field of organic synthesis.

It should, however, be stressed that the vast potentialities of ion-exchange catalysis are still insufficiently exploited in industry. This is not entirely due to the general attachment to conventional methods, for certain shortcomings of ion-exchanger catalysis are also to blame. Their main shortcoming is their rapid decomposition due to chemical or thermal instability. Their high cost and scarcity are also responsible. Finally, the development of ion-exchange catalysis is retarded by lack of cooperation between theory and practice, which is due to obvious underestimations of its great practical possibilities.

This development will undoubtedly be promoted by lower cost, greater variety, and enhanced stability of ion exchangers.

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THE METAL CHEMISTRY OF VANADIUM

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1. METALLIC VANADIUM

Vanadium occurs in Group V of Mendeleev's Periodic System of the elements. Among the metals of industrial importance, vanadium occupies the seventh position, after chromium, in abundance in the Earth's crust, and in this respect considerably surpasses niobium and tantalum, and also molybdenum and tungsten.

The vanadium atom has an unfilled *d* shell, so that vanadium is a transition metal.

The electronegativity series of the metals (according to the "Project for the Nomenclature of Inorganic Compounds" [1]) vanadium occupies an intermediate position, *i.e.* it can be to equal extents an electropositive metal (with respect to metals following it in the electronegativity series) and electronegative (with respect to metals which precede it). This confers on vanadium a special chemical character, and the variety of its chemical compounds is consistent with its position in the electronegativity series of the metals.

Vanadium is among the most difficult of metals to obtain in a pure form. Owing to its great reactivity at high temperatures it gives a series of stable refractory compounds with non-metals. Metallic vanadium is able to absorb considerable quantities of hydrogen. It is only now, when new methods have been developed for preparing vanadium of the highest purity, containing less than 0.05% of impurities, that its physical and mechanical properties can be regarded as firmly established.

Table 1 gives the chemical composition of various grades of vanadium, including both the ductile metal and the brittle, aluminothermic material. To this table should be added the fact that extremely pure vanadium (99.99%) has recently been produced [2] for some new branches of technology. It is prepared in the form of single crystals by the secondary refining of the 99.5% vanadium by methods involving electrolysis, vessel-free zone melting, electron-beam melting, etc. [2]