

ESTERIFICATION OF CARBOXYLIC ACIDS WITH OLEFINS USING CATION EXCHANGE RESINS AS CATALYSTS

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Esterification of acetic acid with α olefins and isobutylene was carried out in the presence of cation exchange resins used as catalysts in the temperature range of 10 to 100°C depending on the nature of the olefin used. Amberlyst 15 showed the highest catalytic efficiency. An attempt was made to separate isobutylene from isomeric butenes by selective esterification with acetic acid.

There are distinct advantages in making isopropyl chloroacetate from propylene and chloroacetic acid; unconverted chloroacetic acid can be recycled using a new strategy.

The transesterification of 2-dodecyl acetate with alcohols such as methanol and n-butanol to give the corresponding ester and secondary alcohol was carried out in the presence of Amberlyst 15 as the catalyst. n-Butanol was found to be a suitable alcohol for this reaction.

INTRODUCTION

The usual method for the preparation of an ester is the reaction of the desired carboxylic acid with the pertinent alcohol in the presence of an acidic catalyst. The direct esterification of olefins and internal olefins is becoming important due to the availability of olefins and internal olefins on a large scale at an attractive price. The esterification of an α -olefin like 1-dodecene with an acid like acetic acid may also provide a route for mak-

ing corresponding secondary alcohols; the direct hydration of higher olefins ($> C_6$) has not been successful so far.

The esters of acetic acid with higher olefins are of commercial importance because of their diverse uses. The esters of lower olefins are used as solvents. The secondary alcohols of higher olefins obtained by transesterification of the corresponding esters are used as solvents for varnishes, inks and for making synthetic detergents. The esters of halogenated carboxylic acids such as chloroacetic acid are also important; e.g., isopropyl chloroacetate is an important intermediate for drugs.

The most common catalysts used for the esterification reactions are strong mineral

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acids, *p*-toluene sulfonic acid, etc. due to their low cost. However they give rise to serious problems such as corrosion and disposal of waste liquor from the reaction mixture. Hence, the use of heterogeneous catalysts such as cation exchange resins has clear advantages since no washing of the catalyst is required [1].

The information available in the literature about the use of ion exchange resins as catalyst for the anhydrous esterification of acids with olefins is limited. Ballentine et al. [2] have carried out a detailed study of the esterification of different carboxylic acids with 1-hexene in the presence of different sheet silicates. They have observed that, in the esterification of acetic acid with 1-hexene in the presence of Cr^{3+} exchanged montmorillonite at 200°C , the product consisted of a 7:3 mixture of 2-hexyl and 3-hexyl acetate. In the literature, it has been reported that dealuminized zeolites can be used as catalysts for the esterification of acetic acid with olefins such as 1-octene and 4-octene to give esters richer in 2-alkylacetate [3,4].

The esterification of acetic acid with 1-butene and 2-butene is generally carried out at elevated temperatures and high pressures. Farbenov et al. [5] have prepared *sec*-butyl acetate by the reaction of acetic acid with 1-butene at 100°C and 9–10 atm pressure in the presence of 10–40 wt.% cation exchange resin. Stepanova et al. [6] have studied the addition of 1-butene and *cis* and *trans* 2-butene to acetic acid to give *sec*-butyl acetate in the presence of sulphonated cation exchanger KU-23 as the catalyst.

Altschul [7] has reported that the equilibrium constant for the esterification of acetic acid with isobutylene at 20°C is 1.82; this drops to 0.59 at 45°C . Gehlawat and Sharma [8] have studied the kinetics of this reaction in the presence of sulfuric acid as the catalyst at 30°C .

Matyschok [9] has studied the reaction of chloroacetic acid with propylene in the pres-

ence of strongly acidic cation exchange resins and has observed that the reaction rates are higher with sulfuric acid than with the cation exchange resins.

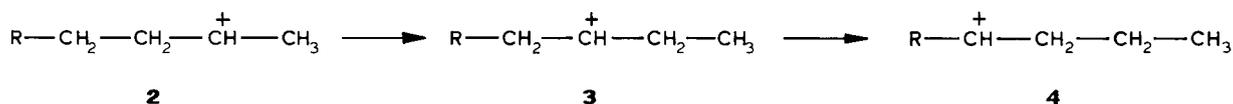
The usual method for the manufacture of secondary alcohols is the direct hydration of the corresponding olefins [10]. In the case of higher olefins ($> \text{C}_6$) however, direct hydration has not been successful so far. The transesterification of esters of higher olefins with lower alcohols provides an easy route for the manufacture of secondary alcohols of the higher olefins. Knof et al. [11] have claimed that secondary alcohols of long chain alkenes can be prepared by the esterification of lower carboxylic acids with long chain α -olefins in the presence of an acidic heterogeneous catalysts such as Amberlyst 15 and transesterification of carboxylate with lower aliphatic alcohols in the presence of an ester exchanging catalyst.

In this paper an attempt has been made to study the kinetics of the esterification of carboxylic acids with olefins in the presence of strong cation exchange resins as catalysts. There are distinct practical advantages to adopting some of the strategies suggested in this paper in practice.

EXPERIMENTAL

Catalyst

The cation exchange resins used were Amberlyst 15 and Amberlyst XN 1010, manufactured by Rohm and Haas Co., U.S.A. and monodisperse K2661 obtained from Bayer, W. Germany. The catalysts were dried at 100°C under vacuum (1–2 mmHg) for 4 hr before use. The physical properties of the cation exchange resins used are given in Table 1.



attacked by the oxygen atom of the hydroxyl group of the carboxylic acid to give an ester.

In the case of higher olefins, the intermediate 2-alkyl carbonium ion can rearrange by hydride shift or by elimination of proton and subsequent reprotonation to give 3-alkyl and 4-alkyl carbonium ions which, on addition with acid, give corresponding alkyl-acetates.

Hence, the number of isomeric ester products that can be obtained in a given reaction is determined by the number of stable carbonium ions which can be formed from an olefin. In the case of isobutylene and isoamylene, alkene oligomerization may compete with the esterification and reaction temperature plays an important role. The synthesis of tert-alkyl acetate fails at temperatures above room temperature due to the rapidity of the oligomerization and the unfavourable thermodynamics, whereas with α -olefins, the esterification reaction is possible only at elevated temperatures due to their poor reactivity.

Effect of catalyst loading

The rate of esterification was found to vary linearly with an increase in the catalyst loading from 2.5 to 10% (w/w). With an increase in the catalyst loading the number of sulfonic acid groups increases, resulting in an increase in the concentration of carbonium ion formed per unit time, which, in turn, increases the rate of reaction.

Effect of speed of agitation

The variation in the speed of agitation from 12 to 40 rev/s had no effect on the rate of reaction. Furthermore, values of the apparent rate constants were well below the calculated

value of the external mass transfer coefficient, based on the correlation developed by Levins and Glastonbury [12]. Hence, it can be concluded that in the range of stirrer speed employed, the reactions are free from external mass transfer resistance.

Effect of particle size

For a specified catalyst loading there was no effect of the variation in the particle size from 0.3 to 0.6 mm on the rate of reaction. This suggests that the diffusional resistance of the reactant in the macropores of the ion exchange resin is not important. This observation was cross-checked with the help of the "interruption test" suggested by Helfferich [13]. The catalyst particles were removed from the reaction mixture for a brief period of time and were then reimmersed. The rate of reaction just after the immersion of the catalyst was the same as that before removing the catalyst from the reaction mixture. This suggests that both diffusion in the macropores and diffusion in the gel phase are not controlling factors.

Kinetic model

The catalysis by ion exchange resin is termed quasi-homogeneous since the catalyst performs its function (in the pores of the resin) by chemical reactions similar to those produced by dissolved acids. Hence, the kinetics of the resin-catalyzed process are basically the same as for reactions catalyzed by homogeneous catalysts. However in formulating the kinetic equation, the distribution of the reactants and the products in the bulk liquid phase and the resin phase (which is the phase where reaction occurs) need to be considered. The order of the reaction was found

to be first order with respect to acid, olefin and ester respectively. The kinetic equation describing the resin catalyzed process can therefore be given as

$$\frac{dC_e}{dt} = k_1\lambda_a C_a \lambda_o C_o - k_2\lambda_e C_e \quad (1)$$

where dC_e/dt = rate of formation of ester, k_1 and k_2 are rate constants for the forward and backward reaction respectively. C_a , C_o , C_e is the concentration of acid, olefin and ester respectively. λ_a , λ_o , λ_e are the distribution coefficients of acid, olefin and ester respectively.

Distribution coefficient

The distribution coefficient of a solute is defined as the ratio of the concentration of the solute in the sorbent and in the solution.

$$\lambda_i = \bar{m}_i / m_i \quad (2)$$

Where λ_i = molal distribution coefficient, \bar{m}_i = concentration of solute in the resin phase, m_i = concentration of solute in the solution.

For practical purposes the distribution coefficient can be calculated from the uptake of solute by the resin phase and is given by the following equation:

$$\lambda_i = \frac{Q_i(100 - w)}{m_i w + \frac{m_i w M_i Q_i}{1000}}$$

where Q_i = uptake of solute in mmol/g of dry resin. w = sorbent content in weight percent, m_i = molecular weight of the solute.

The distribution coefficients were determined by the method suggested by Helfferich [14]. At equilibrium the resin phase was carefully removed from the bulk liquid phase by filtration and the contents of the resin phase were analyzed by the usual analytical procedures. The distribution coefficient for acid, olefin and ester is given in Table 2. It was observed that olefin distributes to a

TABLE 2

Distribution coefficient for the resin catalyzed esterification of acetic acid with 1-dodecene

Temperature = 100 °C

Component	Distribution coefficient
Acetic acid	0.81
1-Dodecene	1.30
Dodecylacetate	1.23

greater extent in the resin phase than acid. This is due to the association of the olefinic π bond with sulfonic acid groups.

Esterification of acetic acid with 1-octene and 1-dodecene

The esterification of acetic acid with 1-octene and 1-dodecene was studied in the temperature range of 80 to 100 °C in the presence of different cation exchange resins such as Amberlyst 15, Amberlyst XN 1010 and monodisperse K 2661. The mole ratio of acid to olefin was varied from 1 : 1 to 4 : 1 to assess its effect on the equilibrium conversion.

Effect of temperature

The effect of temperature on the rates of reaction is shown in Figs. 1 and 2. These reactions were found to be highly temperature-sensitive. At 100 °C, the reaction occurred smoothly and reached equilibrium in about 4 h, but lowering the reaction tempera-

TABLE 3

The forward and backward rate constant for the esterification of acetic acid with 1-octene and 1-dodecene

Temperature = 100 °C

Rate constant	1-Octene ^a	1-Dodecene ^b
k_1 kmol ⁻¹ m ³ s ⁻¹	1.41×10^{-5}	1.23×10^{-5}
k_2 s ⁻¹	9.1×10^{-5}	7.14×10^{-5}

^a 5% (w/w) Amberlyst 15.

^b 10% (w/w) Amberlyst 15.

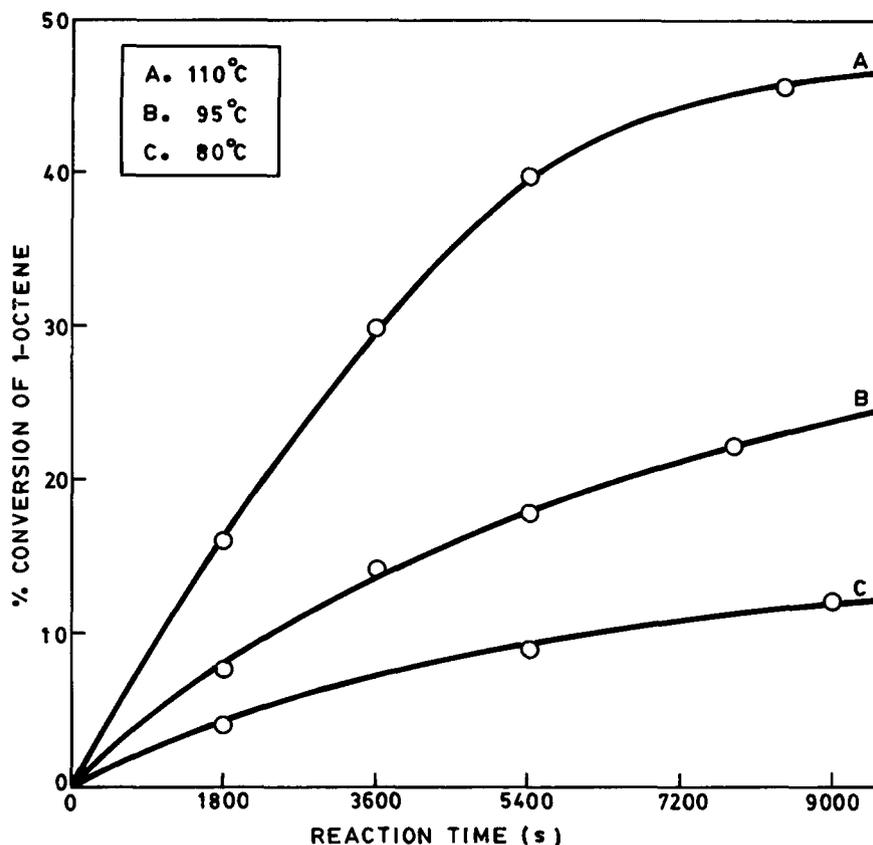


Fig. 1. Effect of temperature on the conversion of 1-octene. Reaction conditions: mole ratio of acetic acid to 1-octene 2:1, catalyst Amberlyst 15 (5% w/w).

ture to 95°C resulted in very low conversion of olefin even after 6 h. The values of the rate constants are given in Table 3 and it is clear that 1-octene is much more reactive than 1-dodecene.

Isomer distribution

The products in the esterification of acetic acid with 1-octene and 1-dodecene were found to contain mainly three isomers 2-, 3-, and 4-alkyl acetate. The authentic samples of the different isomers are not available. Hence the characterization of the different isomers was achieved by gas chromatography according to the method reported by Ballentine et al. [2]. It

was observed that the yield of 2-alkyl acetate goes on decreasing with the progress of the reaction (Fig. 3). At the beginning of the reaction, the yield of 2-alkyl acetate was around 95% (at about 10% conversion of olefin) which dropped to 60% at equilibrium. Once the equilibrium was reached the isomer distribution was not affected by further reaction. Further, the isomer distribution was almost identical in the case of 1-octene and 1-dodecene at the same level of conversion of the olefin under otherwise identical conditions. With a decrease in the reaction temperature from 100 to 95°C, the yield of 2-dodecyl acetate increased from 85 to 93% at about 20% conversion of 1-dodecene. In the pres-

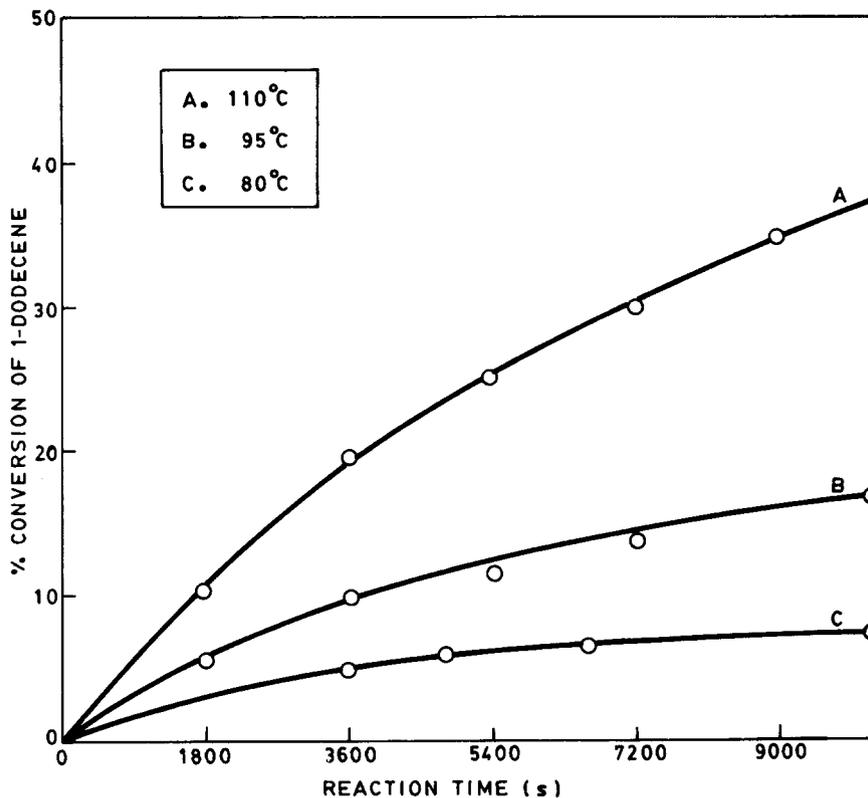


Fig. 2. Effect of temperature on the conversion of 1-dodecene. Reaction conditions: mole ratio of acetic acid to 1-dodecene 2:1, catalyst Amberlyst 15 (10% w/w).

ence of different cation exchange resins, the yield of 2-alkyl acetate was almost identical at the same level of conversion of olefin.

Equilibrium constant

The effect of mole ratio of acid to olefin on the equilibrium conversion in the presence of cation exchange resin and homogeneous catalyst is given in Table 4. When the mole ratio of acid to olefin was greater than one, the homogeneous catalyst (sulfuric acid) gave higher equilibrium conversions than with the cation exchange resin. This difference is due to the fact that the olefin has a tendency to distribute to a greater extent in the resin phase than acid. This results in the lowering of the mole ratio of acid to olefin in the resin phase and shows the equilibrium conversion

corresponding to the reduced mole ratio of acid to olefin. A typical distribution of reactants and the ester in the resin and bulk liquid phase is given in Table 5.

The activity coefficients for the reactants and ester were calculated with the help of the

TABLE 4
Effect of mole ratio on the equilibrium conversion of 1-dodecene
Temperature 100°C

Mole ratio (acid : olefin)	% Equilibrium conversion of 1-dodecene	
	Amberlyst 15 (10% w/w)	Sulfuric acid (2.5% w/w)
1:1	31.7	34.7
2:1	42.1	46.1
4:1	48.3	53.0

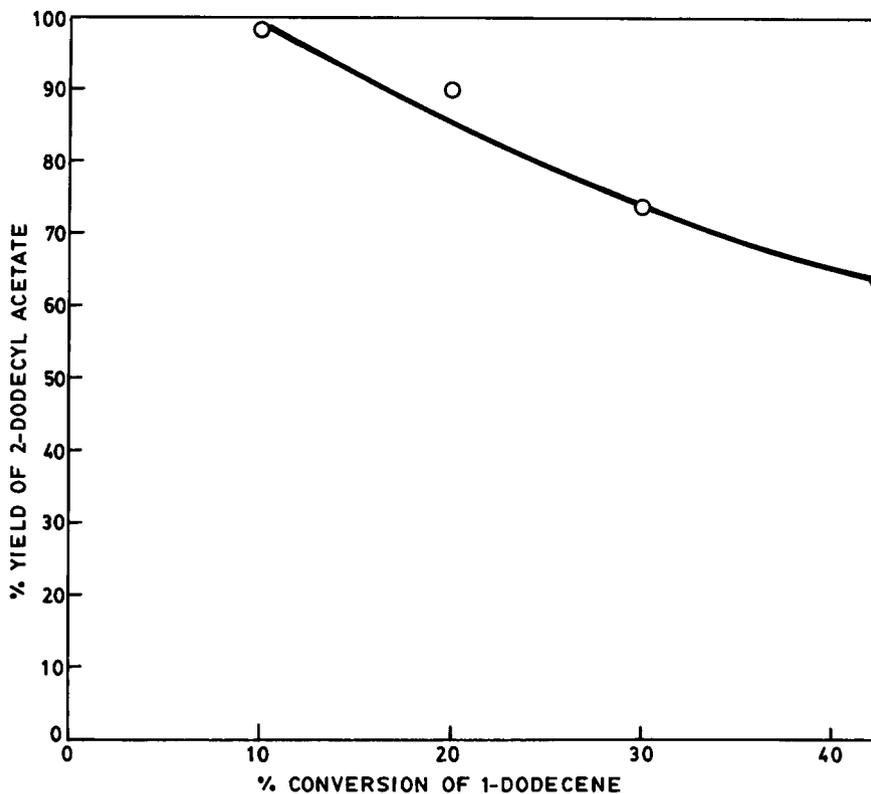


Fig. 3. Effect of conversion of 1-dodecene on the yield of 2-dodecyl acetate. Reaction conditions: mole ratio of acetic acid to 1-dodecene 2:1, temperature 110°C, catalyst Amberlyst 15 (10% w/w).

UNIFAC method [15]. The equilibrium constant based on the activity coefficient and the mole fraction term is given in Table 6.

Comparison of the catalytic activity of different cation exchange resins

The results obtained with different cation exchange resins are shown in Figs. 4 and 5. The comparison of the catalytic activity was made on the basis of the same catalyst loading. The highest reaction rates amongst those resins tried were obtained with Amberlyst 15. Though the difference in the hydrogen ion capacity of Amberlyst 15 and Amberlyst XN 1010 is not substantial (Table 1), Amberlyst 15 showed about 2.66 times more reactivity than Amberlyst XN 1010. In the case of Amberlyst 15, due to moderate degree of crosslinking (20% DVB), most of the sulfonic acid groups are probably in the gel phase,

whereas due to higher degree of crosslinking (85% DVB), in the case of Amberlyst XN 1010, most of the sulfonic acid groups are probably in the surface phase. It is known that sulfonic acid groups in the gel phase can

TABLE 5

Distribution of reactants and product in the resin phase and bulk liquid phase: Acetic acid–1-dodecene–dodecyl acetate system

Mole ratio of acetic acid to 1-dodecene = 2:1; catalyst: Amberlyst 15 (10% w/w); reaction temperature = 100°C.

	Acetic acid	1-dodecene	dodecyl acetate
Bulk liquid phase (mol %)	64.2	23.1	12.7
Resin phase (mol %)	52.7	30.8	16.50

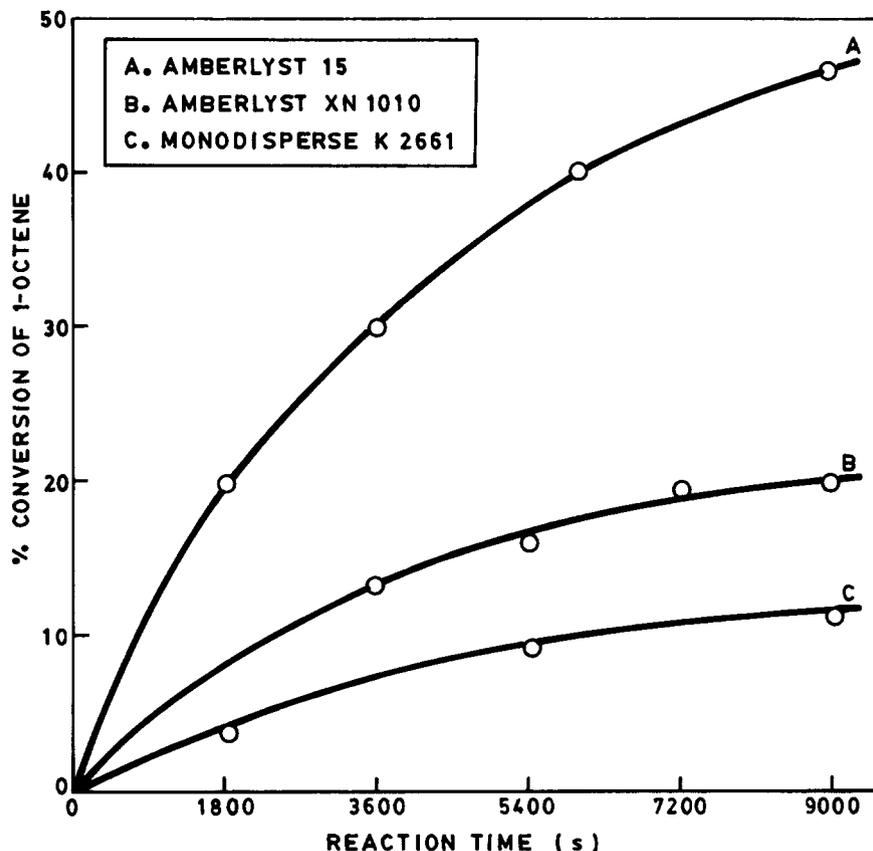


Fig. 4. Effect of different cation exchangers on the conversion of 1-octene, reaction conditions: mole ratio of acetic acid to 1-octene 2:1, temperature 110 °C, catalyst loading 5% (w/w).

be more active than those in the surface phase. This results in a reduction in the catalytic activity of Amberlyst XN 1010. The least

reactivity was shown by monodisperse K2661 and is probably due to its low hydrogen ion capacity. In general, it can be concluded that

TABLE 6

Activity coefficient and equilibrium constant in the resin catalyzed esterification of acetic acid with 1-dodecene^a
Temperature = 100 °C, catalyst: Amberlyst 15 (10% w/w)

Mole ratio (acid/olefin)	x_A	x_o	x_e	ℓ_a	γ_o	γ_e	K (i.e. $k_x k_\gamma$)
2:1	0.526	0.308	0.165	1.111	0.890	0.224	0.231
4:1	0.680	0.174	0.144	1.066	0.942	0.249	0.296

^a x_a , x_e , x_o is mole fraction of acid, ester and olefin respectively. γ_a , γ_o , γ_e is activity coefficient of acid, olefin and ester respectively.

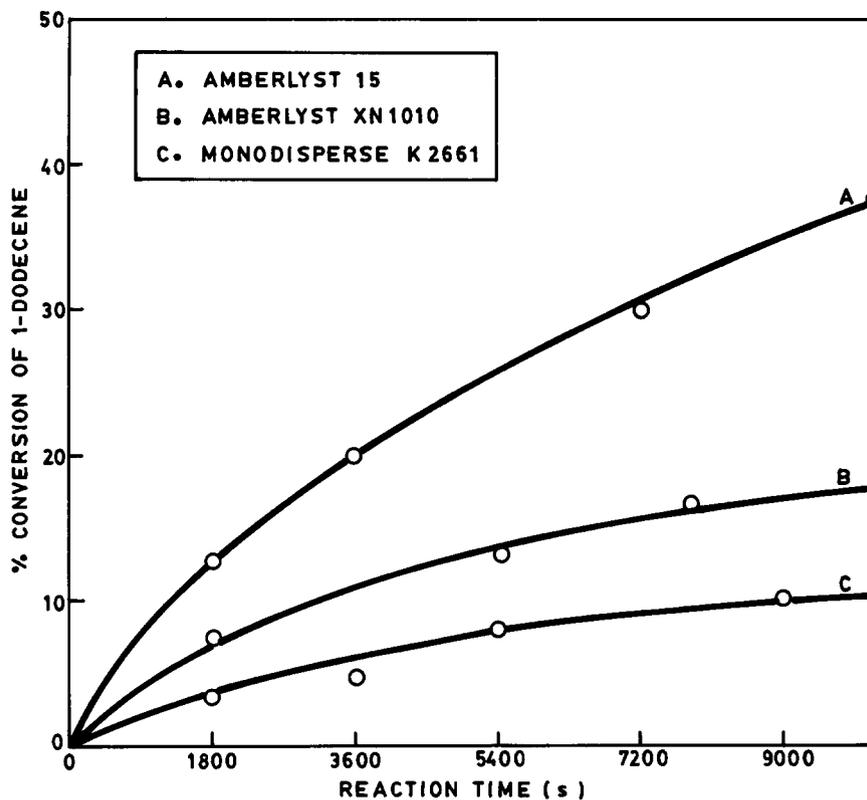


Fig. 5. Effect of different cation exchangers on the conversion of 1-dodecene. Reaction conditions: mole ratio of acetic acid to 1-dodecene 2:1, reaction temperature 110°C, catalyst loading 10% (w/w).

the macroporous resins with lower surface area and higher hydrogen ion capacity are most suitable for this reaction.

Esterification of acetic acid with 1-butene and isobutylene: A new route for the separation of isobutylene from butene

The separation of isobutylene from a butene (isobutylene and 1-butene have practically the same boiling points) mixture is an important industrial problem. The most common method is by selective etherification of isobutylene with methanol in the presence of cation exchange resins as the catalyst [16]. In this work an attempt has been made to achieve separation of isobutylene from a butene mixture by selective esterification with acetic acid.

The reactions were carried out in the temperature range of 10 to 90°C with 10% (w/w) loading of Amberlyst 15. Isobutylene/1-butene was bubbled through the acid-catalyst slurry at atmospheric pressure.

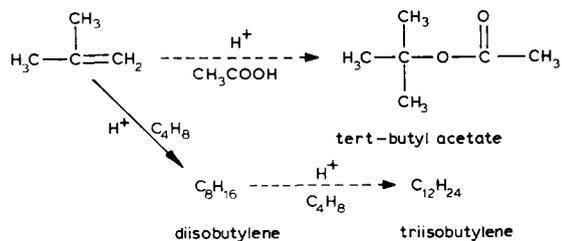
Esterification of acetic acid with 1-butene

The results obtained for this reaction are shown in Fig. 6. At 90°C and at atmospheric pressure, the reactivity of 1-butene was very poor; hence a higher pressure is required for a sizable conversion of acetic acid to sec-butyl acetate.

Esterification of acetic acid with isobutylene

The esterification of acetic acid with isobutylene is accompanied by undesirable

oligomerization reactions as follows:



An increase in the temperature above 20 °C is highly unfavourable for the esterification reaction and oligomerization of isobutylene to diisobutylene/triisobutylene is favoured. The results obtained are given in Table 7.

At a low temperature (10 °C), dimerization of isobutylene was not observed and the yield of tert-butyl acetate based on isobutylene was 100%. With an increase in the reaction temperature to 60 °C, the yield of the ester dropped to 80% and the remainder was mainly diisobutylene (18%). At a higher temperature such as 90 °C, the yield of ester was marginal (18%), that of diisobutylene was 22% and remainder being triisobutylene (60%).

The relative reactivities of isobutylene and 1-butene for the esterification with acetic acid are shown in Fig. 7, from which it is clear that isobutylene can be separated from the

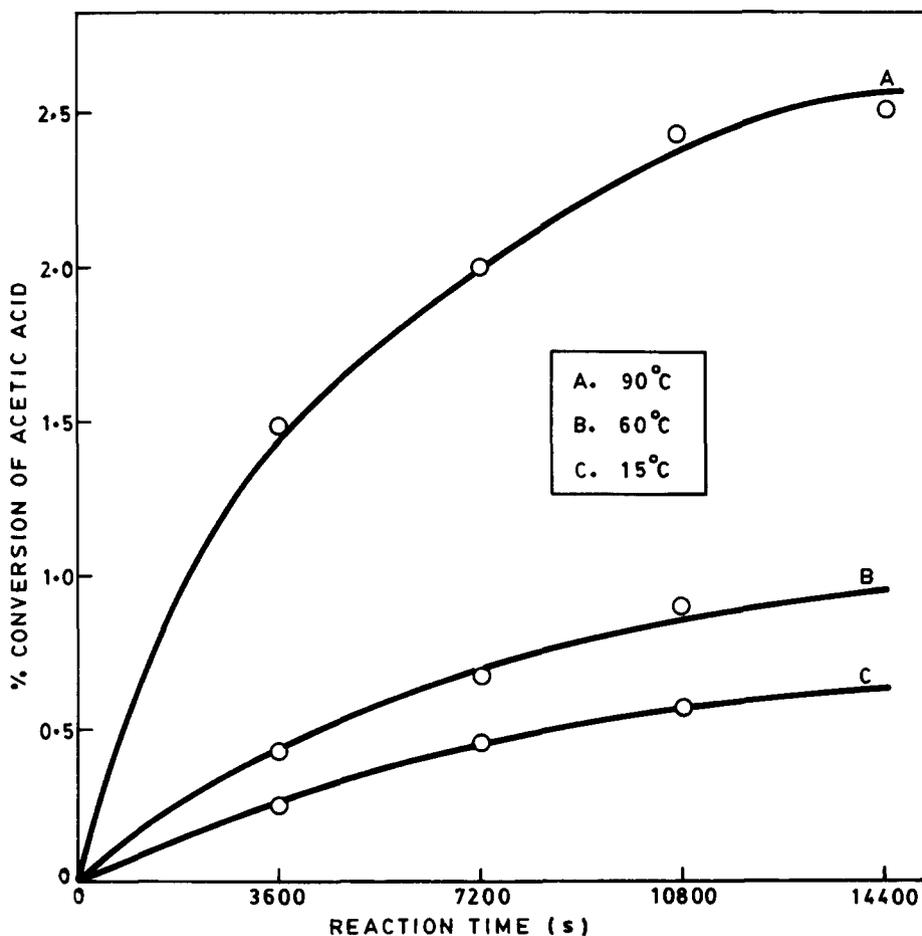


Fig. 6. Effect of temperature on the conversion of acetic acid in the reaction with 1-butene reaction conditions: catalyst Amberlyst 15 (10% w/w).

butene mixture by its selective esterification with acetic acid at lower temperatures.

Esterification of chloroacetic acid with propylene

The manufacture of isopropylchloroacetate is usually based on the esterification of chloroacetic acid with isopropanol in the presence of acidic catalyst. In this method, the removal of water from the reaction mixture is very important and the product specification demands moisture at vanishing levels. This problem can be obviated by the anhydrous esterification of chloroacetic acid with propylene in the presence of cation exchange resin as catalyst.

The esterification of chloroacetic acid with propylene was carried out in the temperature range of 80 to 100°C with 10% (w/w) loading of Amberlyst 15. The results obtained are

given in Figure 8. The use of sulfuric acid as catalyst was much more effective than Amberlyst 15 at about same level of hydrogen ion concentration. But serious problems were faced during the separation of the ester and the recovery of unused acid when sulfuric acid was used as catalyst.

The recovery of unconverted chloroacetic acid and the separation of ester is a very important problem. The ester formed can be easily separated by employing water washes but then the recovery of chloroacetic acid from the aqueous stream becomes difficult. Distillation is another alternative as there exists a large difference in the boiling points of the two. But in this method, decomposition of ester is possible as there is a large proportion of chloroacetic acid in the reaction mixture, which can catalyze the reverse reaction even at lower temperatures. The most suitable method was found to be the extraction of

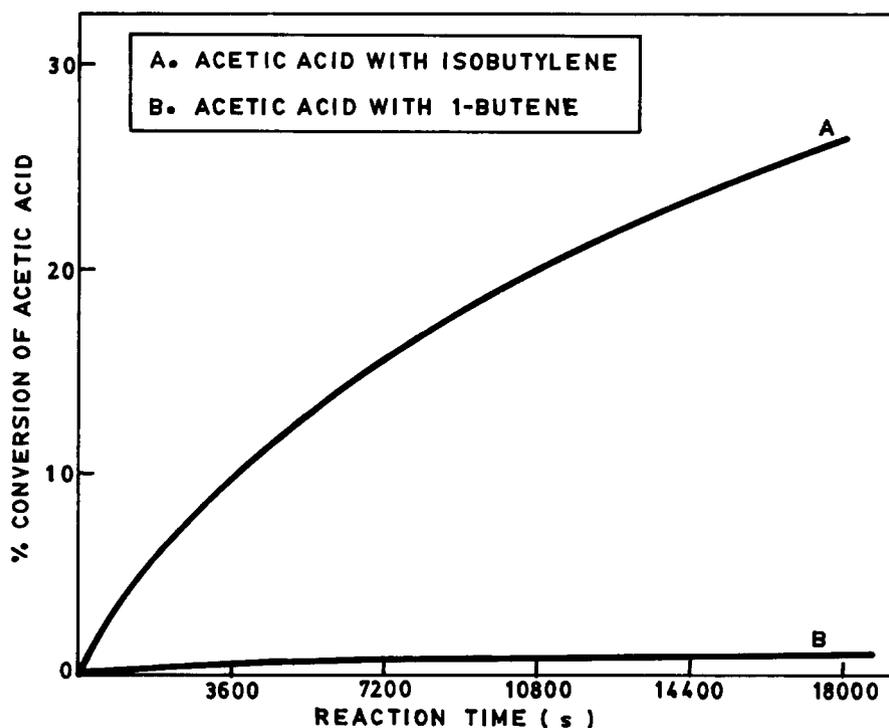


Fig. 7. Relative rates of esterification of isobutylene and 1-butene with acetic acid. Reaction conditions: temperature 10°C, catalyst Amberlyst 15 (5% w/w).

TABLE 7

Esterification of acetic acid with isobutylene ^a

Catalyst: Amberlyst 15 (10% w/w)

Reaction time (min)	10 °C		60 °C		90 °C	
	A	B	A	B	A	B
30	8.9	~100	8.8	80.1	1.5	53.4
60	10.4	~100	–	–	1.9	49.0
90	–	–	13.1	79.9	–	–
120	14.1	99	–	–	2.2	38.2
180	20.0	99	19.9	81.4	3.5	37.8
240	24.5	99	24.9	77.7	3.9	36.1

^a A = % conversion of acetic acid; B = % yield of ester based on isobutylene.

isopropyl chloroacetate in a non-polar solvent followed by recrystallization of chloroacetic acid at lower temperatures.

At the end of the reaction, the reaction mixture was cooled to 0 °C when more than 75% of unconverted chloroacetic acid crystal-

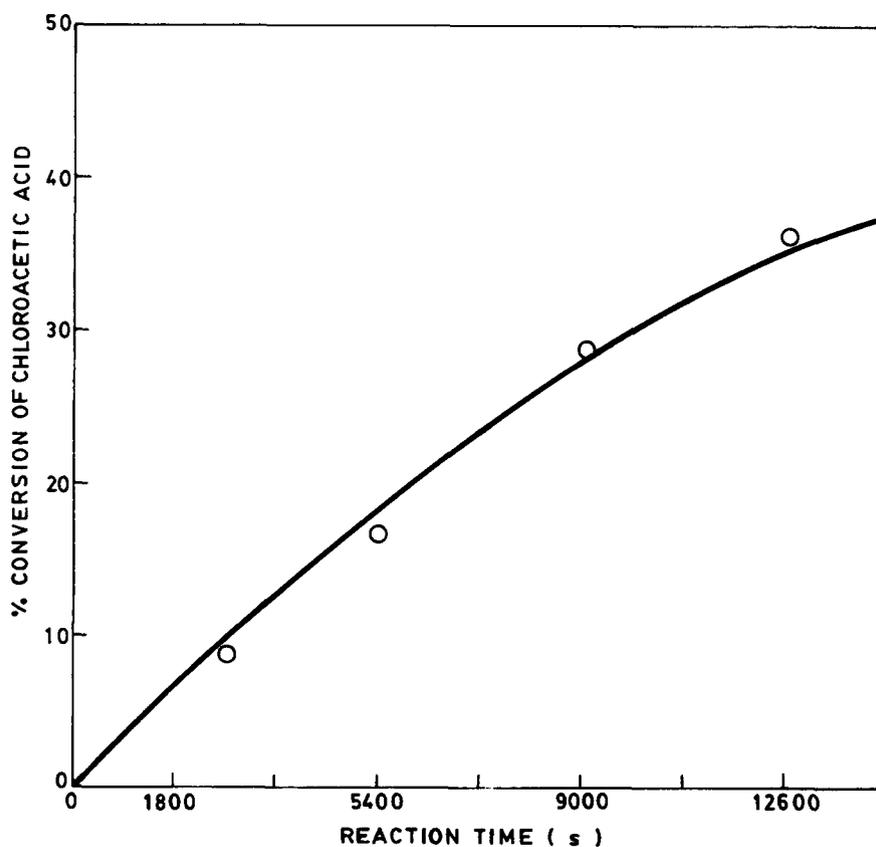


Fig. 8. Esterification of chloroacetic acid with propylene. Reaction conditions: catalyst loading 10% w/w Amberlyst 15, temperature 110 °C.

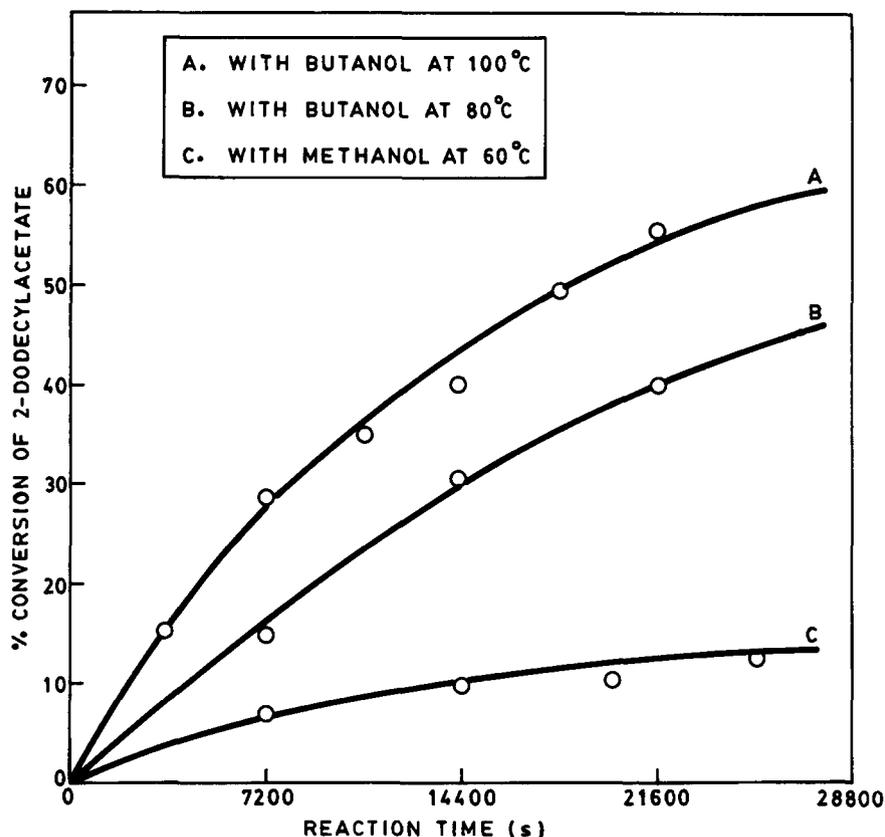


Fig. 9. Transesterification of 2-dodecylacetate to 2-dodecanol. Reaction conditions: mole ratio of alcohol to ester 3:1, catalyst Amberlyst 15 (10% w/w).

lized out; the addition of hexane (at 5°C) allowed the ester to be extracted in the hexane and almost complete (> 96%) recovery of acid was achieved. The ester can be recovered from the hexane phase by distillation at reduced pressure.

Transesterification of 2-dodecyl acetate to 2-dodecanol

The usual method for the manufacture of secondary alcohols is the direct hydration of the corresponding olefin [10]. But in the case of higher olefins (> C₆) direct hydration has not been successful so far. The transesterification of esters of higher olefins with lower alcohols provides an easy route for the manufacture of secondary alcohols of higher

olefins. The catalysts generally used are sulfuric acid, *p*-toluene sulfonic acid, sulfonic acid or metal alkoxides of the corresponding alcohols. The recent trend is to use cation exchange resins in their acid form as it facilitates continuous operation in column type reactor [11].

In the present work, the reactions were carried out with different alcohols in the temperature range of 60 to 100°C. The mole ratio of alcohol to ester was varied from 3:1 to 8:1 to assess its effect on the rate of the reaction. The ester used for this reaction was obtained by the esterification of acetic acid with 1-dodecene at 100°C in the presence of Amberlyst 15 as the catalyst and its composition was 70% 2-dodecyl acetate, 20% 3-dodecyl acetate and the rest 4-dodecyl acetate. The

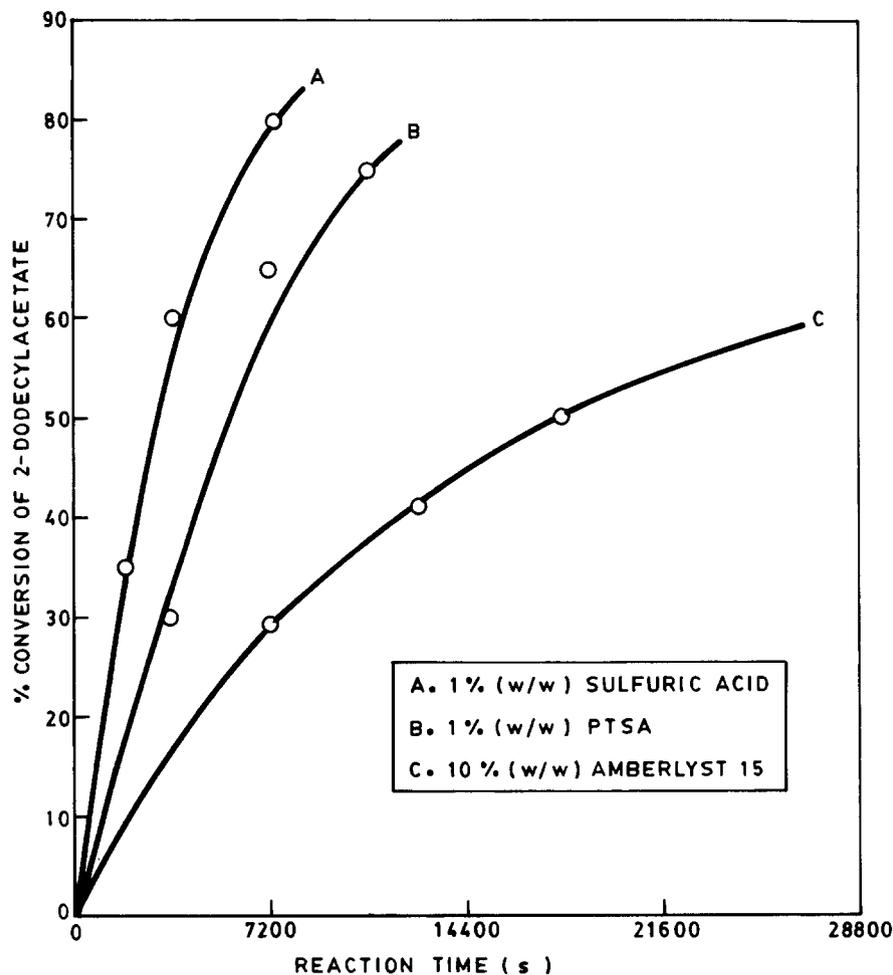


Fig. 10. Effect of different catalysts on the conversion of 2-dodecylacetate. Reaction conditions: mole ratio of butanol to ester 3:1, temperature 100°C.

results obtained are shown in Figure 9. In the case of methanol, even under refluxing conditions very low conversion (10%) of ester to alcohol was obtained even after 4 h, whereas during the same period of time with n-butanol at 100°C about 40% conversion of ester to alcohol was obtained.

The suitability of different catalysts for the reaction was tested and the results are shown in Figure 10. The homogeneous catalysts are more effective than the heterogeneous ion exchange resins and produced more than 90% conversion of ester to alcohol.

CONCLUSIONS

The esterification of carboxylic acids with olefins can be conveniently conducted with strong cation exchange resins as catalyst.

The esterification of acetic acid with 1-octene and 1-dodecene can be smoothly conducted at 100°C. At this temperature the equilibrium constant for 1-dodecene is 0.23 and the yield of 2-dodecyl acetate is about 60% at equilibrium. Amberlyst 15 is the best catalyst amongst those tried.

The separation of isobutylene from butene

mixture can be carried out by the selective esterification of isobutylene with acetic acid at 15°C in the presence of Amberlyst 15 as the catalyst.

The esterification of chloroacetic acid with propylene can be successfully carried out in the presence of cation exchange resin as the catalyst. A novel procedure for the recovery of unconverted chloroacetic acid via crystallization at lower temperature followed by the extraction with hexane can be adopted.

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