Etherification of C_5- and C_8-alkenes with C_1- to C_4-alcohols

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Etherification of two alkenes, 2-methyl-1-butene and 2,4,4-trimethyl-1-pentene, was studied with seven different C_1- to C_4-alcohols. Although etherification was of primary interest, the isomerisation of the alkenes was the main reaction to occur. For the primary alcohols the etherification and isomerisation rates correlated well with the properties of the alcohols. Both rates increased with decreasing polarity and with increasing carbon number, acidity and Mulliken charge of the oxygen atom of the alcohol. It is difficult to distinguish the effect of each property separately, and probably the differences in the reactivities are not due to any one property alone but rather the synergy of the properties affects the reactivities. The secondary alcohols behaved in a different way than the primary ones: the etherification was almost negligible. The effect of alcohol on the isomerisation of alkenes was notable even though alcohol does not directly react in the reaction, which was concluded to be due to the stronger adsorption of the more polar alcohols which hinders the reactions of other components.

KEY WORDS: 2-methyl-1-butene; 2,4,4-trimethyl-2-pentene; etherification; isomerisation

1. Introduction

For some decades now, etherification of alkenes with alcohols has been used as a method to produce fuel components. The first commercially produced tertiary fuel ether MTBE (methyl *tert*-butyl ether, 2-methoxy-2-methylpropane), which is produced from methanol and isobutene (2-methylpropene), is still the most widely used oxygenate in fuel today. Variation in either the alcohol or the alkene has led to the development of many new ether compounds some of which already are in commercial production. Notable among these new compounds are ETBE (ethyl *tert*-butyl ether, 2-ethoxy-2-methylpropane), produced from isobutene and ethanol, and TAME (*tert*-amyl methylether, 2-methoxy-2-methylbutane) produced from methanol and isoamylene (2-methyl-1-butene and 2-methyl-2-butene) [1,2].

In addition, ethanol-based tertiary ethers have been produced from C_5- and C_6-alkenes [3–6], and studies have been made of etherification of C_4- and C_5-alkenes with higher alcohols, mainly propanols and butanol [7–13] but also C_5- to C_{14}-alcohols [14]. Lately, the etherification of C_8-alkenes with methanol has been investigated [15,16].

The interest in MTBE as a fuel component is now beginning to dissipate, as a result of problems that arose in California: MTBE was detected in ground water and its use in the fuel was eventually prohibited [17]. Relative to other gasoline components MTBE is highly soluble in water [1], and owing to its distinct taste and odour it is also detectable in very small concentrations. The unfortunate fate of MTBE has encouraged interest in the study of larger ethers as potential substitute fuel components.

With increasing carbon number of the ether, vapour pressure and water solubility decrease while boiling point increases [1]. Low vapour pressure is advantageous for gasoline blending and low water solubility reduces the risk of water contamination which is the main problem with MTBE. Higher boiling point, in turn, enables the ether to replace some present harmful higher boiling fuel components such as aromatics, the amount of which will need to be reduced to meet tightening regulations. Thus larger ethers are potential fuel components. The benefits of adding of oxygen into the gasoline pool – decreased harmful exhaust emissions and increased octane rating – can be obtained with all these larger ethers [18].

Table 1 presents the published studies of etherification with various alcohols. All of the studies were performed with ion exchange resins as catalysts. Many of the studies focused on the reactivity of one alkene with one alcohol. Etherification of C_5-alkenes has been studied widely with methanol, ethanol and propanols, but any extensive comparison of the effect of various alcohols on the etherification has

Table 1
Some published studies of etherification with various alcohols.

Ref.	Study by	Alkene	Alcohol
[3]	Rihko *et al.*	C_5	MeOH, EtOH
[4]	Linnekoski *et al.*	C_5	EtOH
[5,6]	Zhang and Datta	C_6	EtOH
[7]	Linnekoski *et al.*	C_4	1PrOH, 2PrOH
[8,9]	Ancillotti *et al.*	C_4, C_5	MeOH, EtOH, 1PrOH, 1BuOH
[10]	Kaitale *et al.*	C_4	MeOH, EtOH, 1BuOH
[11]	Solà *et al.*	C_4, C_5	MeOH, 2PrOH
[12]	Calderón *et al.*	C_4	2PrOH
[13]	Cunill *et al.*	C_4	2PrOH
[14]	Macho *et al.*	C_4	MeOH, EtOH, 1PrOH, 2PrOH, 1BuOH, iBuOH, C_5–C_{14} alcohols
[15,16]	Karinen and Krause	C_8	MeOH

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not been published. The most extensive comparisons of various alcohols in table 1 are published by Ancilotti *et al.* [8] and Macho *et al.* [14], but they concentrated on the etherification of isobutene. To the best of our knowledge, etherification of C_8-alkenes has not been studied in detail prior to our studies [15] and the published studies are performed with methanol only.

In this work we extend the existing ether studies by comparing the reactivity of seven different C_1- to C_4-alcohols with two alkenes, 2-methyl-1-butene (2M1B) and 2,4,4-trimethyl-2-pentene (TMP2). Under typical etherification conditions 2-methyl-1-butene is easily isomerised to 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene is isomerised to 2,4,4-trimethyl-1-pentene [19]. The more reactive isomer of each pair [15,20] was chosen for the present study. With isobutene no isomerisation of alkene can be observed, but in our study the structure of the studied alkenes allows also the comparison of the effect of alcohol on the isomerisation of alkenes.

Methanol is by far the cheapest alcohol for use in etherification. Ethanol, in turn, has the environmental advantage that it is produced from renewable biomass rather than fossil fuel. Propanol and butanol isomers were included because it was of interest to study the effect of alcohol structure on the reactivity. Comparison of the behaviour of the various alcohols allows conclusions to be drawn on the reaction mechanism and the effect of reactant properties on the etherification.

2. Experimental

2.1. Reactor

The experiments were carried out in a 80 cm^3 stainless steel batch reactor equipped with a magnetic stirrer and a mixing baffle. The reactor was placed in a water bath by which the temperature of the reactor (60 or 80 °C) was adjusted. The reaction pressure was maintained at 0.8 MPa with nitrogen to ensure that the reaction mixture remained in the liquid phase. The catalyst, 1.0–1.5 g, was placed in a metal gauze basket. Samples were taken from the reaction mixture manually via a sample valve at the top of the reactor.

2.2. Chemicals

The reactants were 2-methyl-1-butene (Aldrich, >99%), 2,4,4-trimethyl-2-pentene (Fluka Chemica AG, >98%), methanol (99.8%, Riedel–de Haën), ethanol (99.5%, Primalco Oy), 1-propanol (99.5%, Riedel–de Haën), 2-propanol (99.99%, Fisher Scientific), 1-butanol (99.5%, Riedel–de Haën), isobutanol (2-methyl-1-propanol, 99%, Riedel–de Haën), and 2-butanol (>99%, Riedel–de Haën). Isooctane (2,2,4-trimethylpentane, Merck, >99.5%) was used as an inert solvent in the TMP2 experiments and nitrogen (Aga, 99.5%) was used for pressurisation of the reactor.

2.3. Catalyst

Commercial Amberlyst ion exchange resins (Rohm & Haas) were used as catalysts. Amberlyst 15 (H^+ 4.7 eq/kg) was used in the C_5 experiments and Amberlyst 35 (H^+ 5.2 eq/kg) in C_8 experiments. Before the experiments the catalysts were washed with alcohol to remove moisture from the pores. Water must be removed as completely as possible before the reaction because it readily reacts with alkenes to form tertiary alcohol. In addition to accelerating undesired side reactions, water also inhibits the etherification reaction and decreases the selectivity towards ether [21,22]. After the experiment the catalyst was dried and the mass of the dry catalyst was used in calculations.

2.4. Analytical methods

Samples were analysed with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a capillary column DB-1 (J&W Scientific, length 60 m, film thickness 1.00 μm, diameter 0.250 mm) and a flame ionisation detector. The products were quantified by internal standard method.

2.5. Calculation

The initial rates are interpolated from the curves of molar amount (mmol) of ether or alkene formed as a function of contact time (time × mass of the catalyst ($h\,g_{cat}$)). The etherification rate refers to the formation of ether from the alkenes, the isomerisation rate to the double bond isomerisation of alkene to its isomer (2M1B to 2M2B or TMP2 to TMP1), and the total rate to the total consumption rate of the original alkene (etherification + isomerisation). The ratio of isomerisation to etherification (I/E ratio) is defined as the initial rate of isomerisation divided by the initial rate of etherification.

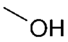
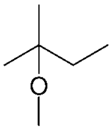
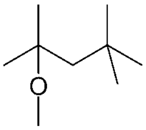
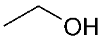
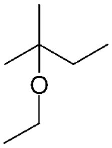
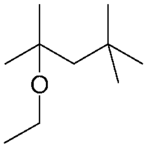
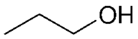
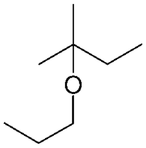
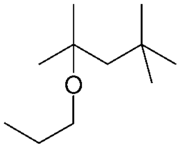
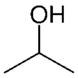
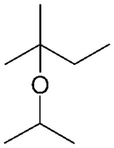
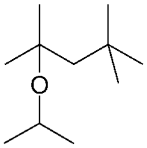
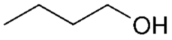
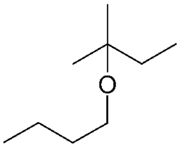
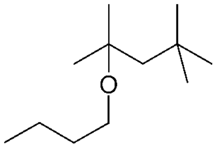
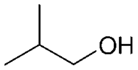
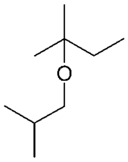
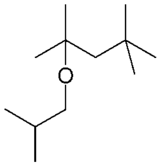
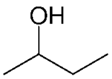
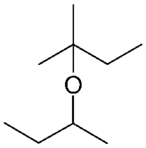
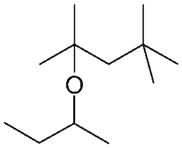
3. Results and discussion

The ethers produced from 2M1B and TMP2 with various alcohols are presented in table 2. In addition to etherification also isomerisation occurs in the reaction mixtures: 2-methyl-1-butene is isomerised to 2-methyl-2-butene and 2,4,4-trimethyl-2-pentene to 2,4,4-trimethyl-1-pentene. In fact, under the studied conditions the double bond isomerisation was the main reaction to occur with all alcohols except methanol.

The alcohols of the study can be divided into two groups according to their structure, *i.e.*, into primary and secondary alcohols: 2PrOH and 2BuOH are secondary alcohols and the others are primary. Tertiary butanol (2-methyl-2-propanol) is not reactive in etherification [14] and was not included in our experiments.

The initial rates of each reaction and the ratio of isomerisation to etherification (I/E ratio) are presented in tables 3 and 4. As a general trend the rates increase towards larger alcohols, which has been observed earlier [8,14], but there are,

Table 2
The formed ether molecules.

Alcohol	Ether from 2M1B	Ether from TMP2
 methanol (MeOH)	20  2-methoxy-2-methylbutane (TAME)	 2-methoxy-2,4,4-trimethyl-pentane
 ethanol (EtOH)	 2-ethoxy-2-methylbutane (TAEE)	 2-ethoxy-2,4,4-trimethylpentane
 1-propanol (1PrOH)	 2-methyl-2-propoxybutane	 2,4,4-trimethyl 2-propyloxy-pentane
 2-propanol (2PrOH)	 2-isopropyloxy-2-methyl-butane	 2-isopropyloxy-2,4,4-trimethyl-pentane
 1-butanol (1BuOH)	 2-butoxy-2-methylbutane	 2-butoxy-2,4,4-trimethylpentane
 isobutanol (iBuOH)	 2-isobutyloxy-2-methylbutane	 2-isobutyloxy-2,4,4-trimethyl-pentane
 2-butanol (2BuOH)	 2-methyl-2-(1-methyl-propyloxy)butane	 2,4,4-trimethyl-2-(1-methylpropyloxy)pentane

however, some exceptions. With the primary alcohols the etherification rate increases as a function of the carbon number of the alcohol, but with the secondary alcohols (2PrOH and 2BuOH) the etherification rate is much slower, almost negligible compared with that for the primary alcohols with the same carbon number. The rate of isomerisation increases with the carbon number of the alcohol, but the effect is only indirect, since alcohol is not a reagent in the isomerisation reaction of alkenes. The total rate of consumption of the alkene (etherification + isomerisation) increases with size of

Table 3
Initial rates of etherification and isomerisation for 2M1B (mmol/(h g_{cat})).

	Etherification		Isomerisation		Total rate		I/E ratio	
	60 °C	80 °C	60 °C	80 °C	60 °C	80 °C	60 °C	80 °C
MeOH	110	320	50	150	160	470	0.5	0.5
EtOH	100	340	100	370	200	710	1.0	1.1
1PrOH	120	183	170	331	290	514	1.4	1.8
2PrOH	9	37	82	535	91	572	9.3	14.3
1BuOH	138	366	223	613	360	979	1.6	1.7
iBuOH	174	467	213	767	386	1234	1.2	1.6

Table 4
Initial rates of etherification and isomerisation for TMP2 (mmol/(h g_{cat})).

	Etherification		Isomerisation		Total rate		I/E ratio	
	60 °C	80 °C	60 °C	80 °C	60 °C	80 °C	60 °C	80 °C
MeOH	0.4	2.1	0.3	3.0	0.7	5.1	0.9	1.4
EtOH	0.4	1.3	0.9	7.4	1.3	8.7	2.4	5.6
1PrOH	0.6	1.9	2.5	17.8	3.2	19.7	4.0	9.2
2PrOH	3×10^{-2}	0.2	2.3	20.6	2.3	20.8	67.1	106.3
1BuOH	1.0	2.5	5.7	29.1	6.7	31.5	5.9	11.8
2BuOH	0.1	0.1	6.5	32.0	6.6	32.2	45.9	215.9
iBuOH	1.2	2.3	7.5	29.5	8.7	31.8	6.5	12.7

the alcohol, and, interestingly, for TMP2 the total rate is almost the same for alcohols of the same molecular size, even though etherification is extremely slow in the presence of the secondary alcohols. It is also worth noting that within the primary butanols the reaction rates with isobutanol were higher than with 1-butanol, and thus branching and the steric effects do not limit the reactivity with primary butanols.

The reaction rates of C_5-alkenes cannot be compared with the rates of C_8-alkenes as such because of the different dilutions in the reaction mixture and the somewhat different catalysts used in the experiments. Furthermore, we have demonstrated in our previous work that the etherification reaction of C_8-alkenes on the ion exchange resin is limited by internal diffusion [23]. It is nevertheless evident that the reaction rates decrease dramatically with increase in the carbon number of the alkene. The ratio of isomerisation to etherification (I/E ratio) is also affected: the ratio is higher with TMP2, which indicates that relatively more alkene is consumed in the etherification reaction with 2M1B than with TMP2. With the exception of methanol, the numeric value of this ratio is greater than unity for both alkenes and thus isomerisation is the main reaction to occur.

The reaction equilibrium was not studied within this work. In the etherification of isobutylene with various alcohols it has been shown that the reaction equilibrium constant decreases with increasing size of the alcohol. *E.g.*, at 50 °C the equilibrium constant for the etherification of isobutene is 79 with methanol [24], 40 with ethanol [24], 30 with 1-propanol [7] and 2.6 with 2-propanol [7].

3.1. The properties of the alcohols

Because the trends for the two alkenes as a function of the alcohols are generally the same, it is reasonable to focus the discussion on the effect of the various alcohols to determine how the properties determine the reactivity. The reaction rate cannot be explained solely on the basis of the molecular size of the alcohol. Contrary to alkenes, the size of the alcohol molecule does not decrease the reaction rate, and thus the differences in the nature of the alcohols encouraged us to study other properties of the alcohols, and for this purpose, selected properties of the alcohols are listed in table 5. In addition to the molecular size of the alcohol, we chose to compare the alcohols by studying the effect of acidity and polarity of alcohol on their reactivity, because these properties have been presented to affect the etherification mechanisms, reactivity of alcohols and ion exchange resin catalysts [9,25,26]. Finally, the reactive oxygen atom of the alcohol was studied by the Mulliken atom charge to find out how the reactivity of the alcohol is affected by the charge of the oxygen atom and to study if the reactivity of alcohol could be predicted by estimated properties.

Table 5
Properties of the alcohols.

	ε	pK_a	Mulliken charge
Methanol	32.6	15.1	−0.726
Ethanol	24.3	15.9	−0.734
1-propanol	20.1	16.1	−0.741
2-propanol	18.3	17.1	−0.743
1-butanol	17.8	16.1	−0.741
2-butanol	15.8	17.6	−0.750
Isobutanol	17.7	16.1	−0.745

The dielectric constants ε [27], which are a measure of polarity of a liquid, and the pK_a values for acidities [28] were obtained from the literature and the Mulliken atomic charges of the alcohols were calculated by PC Spartan Pro software (Wavefunction Inc.). The calculations were performed with the Hartree–Fock model with the 6-31G* basis set.

Comparison of the carbon numbers, dielectric constants, pK_a values and Mulliken charges of the alcohols presented in table 5 reveals a strong correlation between the properties. Thus, it is difficult to distinguish the effect of each property separately. Probably, the changes in the reactivities are not due to any one property alone but to the synergy of the properties. Although the studied properties may to some extent describe the same phenomena, it is justified to look at all the properties and to determine how well the experimentally measured properties (pK_a and ε) interpret the results relative to estimated properties (Mulliken atomic charges).

3.2. Effect of polarity

The dielectric constant ε is a measure of how well a solvent reduces the interactions between ions in solution: ions dissolved in a polar solvent exhibit weaker interaction with other ions than do ions dissolved in a less polar solvent [29]. Components with dielectric constants larger than 15 are regarded as polar components [29], which means that all of the present alcohols can be classified as polar. As can be seen from table 5, ε decreases with carbon number, and the reaction rates decrease with increasing ε.

With methanol, which has the highest ε of the alcohols studied, the total rate of alkene consumption is low (see figure 1). Ethanol is less polar and the reaction rate is faster. As a move is made along the homologous series of alcohols to 1-propanol and 1-butanol the dielectric constant further decreases and the total rate of alkene consumption increases. The inhibiting effect of methanol on the reaction rate has been detected in many studies [15,30].

The inhibiting effect can be explained in terms of polarity. In a reaction mixture, polar components are preferred in adsorption over the less polar components [31]. The more polar the alcohol is, the stronger is its adsorption on the ion exchange resin and the larger is its adsorption constant. Thus the reactions involving alkenes are suppressed in the presence of the most polar alcohols. This also explains why the isomerisation is so strongly affected by alcohol: in the case of the more polar alcohols isomerisation is limited by the small amount of alkene on the catalyst. With the decreasing polarity of the reaction mixture more and more alkene reaches the catalyst and the etherification rate and especially the isomerisation rate increase. The limiting case is a reaction mixture where no alcohol is present. It was observed that the reaction rate in the presence of isobutanol approaches the rate in the total absence of polar components, *i.e.*, pure isomerisation [19], although in the presence of isobutanol the thermodynamic equilibrium between the 2,4,4-trimethylpentene isomers is not reached as fast as without polar components in the reaction mixture. However, this comparison allows us to conclude that the polarity of the reaction mixture has a strong effect on the reaction rate, which most probably is due to the stronger adsorption of the more polar components on the ion exchange resin resulting in a suppression of reactions involving less polar components, like alkenes.

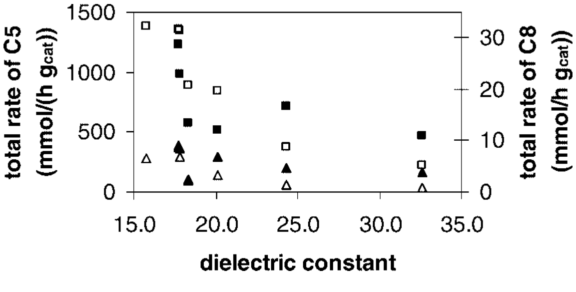


Figure 1. Total reaction rate of alkenes as a function of the dielectric constant of the alcohol: (▲) C_5 60 °C, (■) C_5 80 °C, (△) C_8 60 °C and (□) C_8 80 °C.

The inhibiting effect of alcohol might also be explained by the effect of the polarity of the reactants on the ion exchange resin catalyst. When no polar components are present to affect the resin, the polymer-bound highly active sulfonic acid groups ($-SO_3H$) act as the active catalytic sites. In the presence of more polar reaction medium the $-SO_3H$ groups dissociate, and solvated protons, which are relatively less active, become the catalytic agents [32]. Here, the most polar alcohol, methanol, decreases the activity of the catalyst most, and the activity and reaction rate increase with a shift towards decreasing polarity of the alcohols (see figure 1).

It has been claimed that a certain polarity is demanded to swell the pores of the ion exchange resin catalyst to improve the accessibility of the active catalytic sites [32,33]. Since the total rate is increasing with decreasing polarity of alcohol, it can be concluded that each of the studied alcohols is polar enough to swell the pores of the catalyst and the accessibility of the active sites of the catalyst is not limiting the reaction rate.

3.3. Effect of the acidity of the alcohol

As seen in table 5, the pK_a value, which is a measure of the acidity of a compound, exhibits a slight increasing trend as a function of the molecular size of the alcohol. There is one very striking feature, however: the pK_a values of the secondary alcohols are larger than those of the primary alcohols. It should be noted that the scale of the pK_a values is not very large ($15.1 \rightarrow 17.6$, $\Delta pK_a = 2.5$) but it should also be remembered that the pK_a values are presented in logarithmic scale. Thus relatively small changes in numerical values of pK_a result in marked change in the behaviour of the alcohol.

The smaller the pK_a value, the stronger is the acid. In general, the acidity order of the substituted alcohols is primary > secondary > tertiary [34]. The main difference in the reactivity of the alcohols we studied was that the I/E ratio was substantially larger with the less acidic secondary alcohols. In the presence of more acidic alcohols alkenes undergo more etherification and in the presence of less acidic alcohols they undergo more isomerisation, as presented in figure 2 for the primary alcohols.

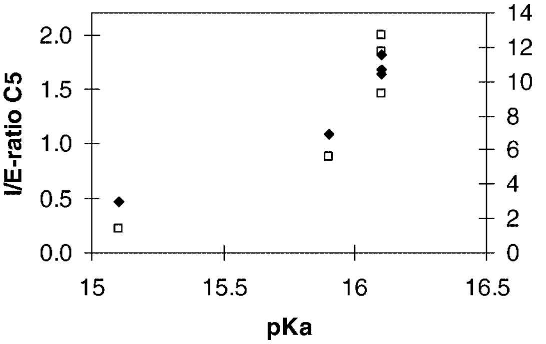


Figure 2. I/E ratio for the primary alcohols at 80 °C as a function of acidity of the alcohol: (◆) C_5 and (□) C_8.

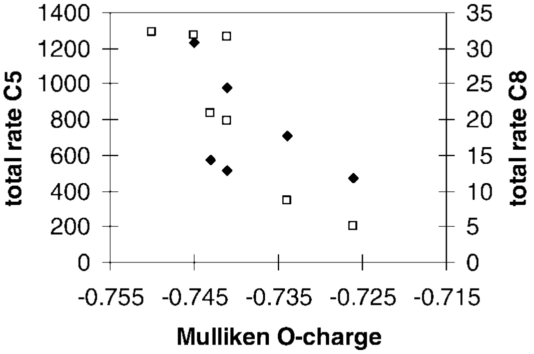


Figure 3. Total rate at 80 °C as a function of the Mulliken charge of the oxygen atom of the alcohol: (◆) C_5 and (□) C_8.

In the presence of acids alcohols undergo protonation. It has been proposed that the etherification mechanism includes protonation of alcohol, *e.g.*, [8]. If this is indeed so, then the rate should be faster when the protonation of the alcohol is easier. A less acidic alcohol reacts more easily with the sulfonic acid groups and forms protonated alcohol. From table 5 we can see that among the primary alcohols the acidity decreases as a function of molecular size, which is also the trend of increasing reactivity.

Acidity of protonated primary alcohols is reported to increase in the order $\mathrm{MeOH}_2^+ < \mathrm{EtOH}_2^+ < 1\mathrm{PrOH}_2^+ < 1\mathrm{BuOH}_2^+$ [35]. In our experiments we see that the total reaction rate increases with the acidity of the protonated alcohol, which indicates that the more acidic protonated alcohol reacts more easily with alkenes. Most of the total reaction rate is due to the isomerisation of the alkene, and alcohol does not directly take part in this reaction. The effect of alcohol on the isomerisation rate could also be explained by reaction mechanism where the activation of alkene towards reaction involves interaction with the protonated alcohol, and only after this the alkene reacts further. This would explain why the properties of the alcohol also influence the alkene isomerisation reaction, but the inhibition of reactions involving alkenes by the adsorption of the more polar components explained above seems more likely in this case.

The secondary alcohols are the less acidic, and thus they should react with the alkenes faster than do the primary alcohols; however, the total reaction rates of the alkenes are not much faster with the secondary than with the respective primary alcohols. The reason for this is the negligible etherification rate with the secondary alcohols. The etherification is perhaps sterically hindered in some way and the almost total absence of etherification reduces the total rate.

3.4. Effect of the Mulliken atomic charge of the oxygen atom

Finally, the behaviour of the alcohols was compared as a function of the Mulliken atomic charges. The atomic charge itself is not a straightforward concept since it cannot be measured. However, computational methods allow the atomic charges to be estimated [36]. Mulliken has introduced the Mulliken population analysis which allows the calculation of the Mulliken charges. The atomic charge illustrates the distribution of the electronic population among the atoms in the molecule [37]. We calculated the atomic charge of the oxygen atom of the alcohol (see table 5) to determine whether this charge has an influence on the reactivity of the alcohol.

We observed that the more negative the charge of the oxygen atom the higher was the total reaction rate as plotted in figure 3. This is entirely reasonable, since the more negative the charge of the oxygen atom, the more readily it accepts a positively charged proton and protonates. This also nicely supports the conclusions drawn on protonation as a function of acidity. Also the I/E ratio is increased as a function of the Mulliken charge in a similar way as with the acidity. However, the differences between the reactivity of primary and secondary alcohols cannot be explained with the Mulliken charge.

3.5. Estimation of the reactivity by the properties of alcohols

It was observed that the primary alcohols exhibit clear trends as a function of the studied properties: the reaction rate increased with increasing carbon number and acidity and with decreasing polarity of the alcohol. The secondary alcohols behaved differently, as their etherification rate was almost negligible compared to the primary ones. As tertiary butanol is not reactive in etherification [14], it can be concluded that the structure of the alcohol affects its reactivity: the primary alcohols are reactive in etherification and the reactivity is markedly decreased when shifted to secondary alcohols, and finally, the tertiary alcohols do not react with alkenes.

The most important finding of this study was that the alcohol affects the isomerisation rate, although it does not directly react in the isomerisation reaction. Few explanations for the strong effect of alcohol on the isomerisation were proposed, and the most probable one is the stronger adsorption of the more polar components on the ion exchange resin which hinders the access of the other components to the catalyst and the reactions involving alkenes are suppressed due to the lack of alkene molecules on the catalyst. Furthermore, the polarity of the reaction mixture has an effect on the catalyst. In addition to swelling the catalyst, the polarity of the reaction mixture affects the active catalytic sites, and the nature of the catalytic sites may vary as a function of polarity of the reaction mixture. The activity of the ion exchange resin catalyst was observed to decrease with increasing polarity of the reaction mixture.

The activation of the alcohol towards reaction most probably involves protonation. The protonation of less acidic alcohols is easier, which leads to increasing reaction rate as a function of decreasing acidity.

The studied properties of alcohols can be used to explain the trends observed in the reactivities and reaction rates. It is, however, difficult to distinguish the role of each property, since they seem to affect very similarly on the reaction rates and they may to some extent describe the same phenomena. Probably the differences in the reactivities of alcohols are not due to any one property of the alcohols alone but to the synergy of the properties. However, we can conclude that general trends of reactivities of the alcohols in etherification reaction can be predicted from their properties. Detailed study of the reaction mechanism will, however, require more experimental information and modelling of the reactions.

4. Conclusions

Etherification of two alkenes, 2-methyl-1-butene and 2,4,4-trimethyl-1-pentene, was studied with seven different C_1- to C_4-alcohols, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol and isobutanol. Although etherification was the reaction of interest, the main reaction to occur was isomerisation of the alkenes, and the isomerisation to etherification ratio varied as a function of alcohol.

With the primary alcohols the etherification and isomerisation rates increased with increasing carbon number and acidity and with decreasing polarity. Reaction rates were also studied as a function of an estimated property of the alcohols: the Mulliken charge of the oxygen molecule. The experimental results as a function of the Mulliken charge supported well the results and trends obtained as a function of acidity. The secondary alcohols behaved differently from the primary alcohols: the etherification was negligible but the isomerisation reaction was as fast as with the primary alcohols.

The effect of the alcohols on the isomerisation of the alkenes was marked even though the alcohol does not itself take part in the reaction. This was explained in terms of polarity: in a mixture the adsorption of more polar components is preferred. Thus the very strong adsorption of the most polar alcohols, like methanol, hinders the access of the other components to the catalyst and the reactions involving alkenes are suppressed due to the lack of alkene molecules on the catalyst.

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