A novel tertiary ether. Synthesis of 3-methoxy-3-methylheptane from 2-ethyl-1-hexene and methanol

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2-ethyl-1-hexene was etherified with methanol to 3-methoxy-3-methylheptane. The product ether is a novel compound whose existence has not been reported earlier. Isomerisation of 2-ethyl-1-hexene leads to four alkenes, and each of these produces the same ether compound. In a study of the conditions for the etherification reaction it was observed that the ether formation can be maximised by decreasing the temperature and increasing the molar ratio of methanol to 2-ethyl-1-hexene. This is what would be expected for an exothermic reaction controlled by thermodynamic equilibrium.

Keywords: tertiary ethers, etherification, oxygenates

1. Introduction

Oxygenates are typical oxygen-containing components of reformulated gasoline. Oxygen changes the air to fuel ratio so that the fuel burns more cleanly, and exhaust emissions are reduced. MTBE (methyl *tert*-butyl ether, 2-methoxy-2-methylpropane) has for many years been the most widely used oxygenate in reformulated gasoline, but recent troubles over the discovery of MTBE in ground water in California are likely to change the situation. MTBE is highly soluble in water and when it comes in contact with the ground it travels through the soil all the way to the ground water, where it is easily detected due to its distinct odour and taste even in very low concentrations. MTBE degrades very slowly in soil and ground water, and it has now been decided that by the end of the year 2002 MTBE will no longer be allowed in gasoline sold in California [1].

In some countries, regulations concerning the composition of gasoline determine the minimum oxygen content in the gasoline. If oxygen is still required in gasoline in the future, new oxygenates will have to be available where use of MTBE is prohitibed. Since oxygen has proved to have an advantageous effect in gasoline, it is reasonable to assume that it will still be required in gasoline in the future, or at least commonly used. Potential oxygenates for gasoline components are alcohols and larger ethers with lower water solubility than MTBE.

Alcohols such as ethanol, are not ideal components in gasoline due to their high vapour pressures: high vapour pressure leads to increasing emissions and the advantages in exhaust emissions gained by adding oxygenates to the gasoline pool are lost [2]. Furthermore, the high water solubility, and especially the separation of organic and water phases at low temperature, complicate the use of ethanol in fuel [2,3]. In this respect, alternative higher ethers, which are compounds produced from either higher alcohols or higher alkenes, are far more suitable oxygen sources in gasoline. The water solubility of an ether can be expected to decrease with increasing molecular weight [4]. Higher ethers also have higher boiling points, which enables them to replace aromatics in the gasoline pool. Ethers such as ETBE (ethyl *tert*-butyl ether, 2-ethoxy-2-methylpropane) and TAME (*tert*-amyl methyl ether, 2-methoxy-2-methylbutane) are already being incorporated in reformulated gasoline. TAME and some heavier ethers, *tert*-hexyl methyl ether and *tert*-heptyl methyl ether, have proven to be as good gasoline components as MTBE [5].

In recent work [6] we studied the activity of 2,4,4-trimethylpentenes and 2-methylheptenes in etherification with methanol. This work extends the studies of reactivity of C_8-alkenes with methanol by examining the reactions of 2-ethyl-1-hexene and its isomers to produce 3-methoxy-3-methylheptane. The recently quite widely studied family of tertiary ethers hereby obtains a new member, since this particular ether compound, 3-methoxy-3-methylheptane, evidently has not been reported prior to our studies [7]. 3-methoxy-3-methylheptane is a totally new molecule.

2. Experimental

2.1. Reactor

The experiments were carried out in an 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 means of which the temperature of the reactor (50–90 °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 was placed in a metal gauze basket.

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2.2. Catalyst

The catalyst was a commercial Amberlyst 35Wet (5.2 eq/kg, Rohm & Haas), which is a macroreticular, cationic, strongly acidic ion exchange resin. Before the experiments the catalyst was washed with methanol to remove moisture from the pores. Water must be removed from the catalyst as thoroughly as possible before the reaction because it readily reacts with alkenes to form tertiary alcohol. In addition to accelerating the undesired side reactions, water also inhibits the etherification reaction and decreases the selectivity towards ether [8,9]. After the experiment the catalyst was dried and the mass of the dry catalyst was used in calculations.

2.3. Chemicals

The reactants were methanol (Riedel–de Haën, $>$99.8%) and 2-ethyl-1-hexene. The synthesis of 2-ethyl-1-hexene has been published elsewhere [10]. The reactants were diluted with toluene (Riedel–de Haën, $>$99.7%), and isooctane (Merck, $>$99.5%) was used as an internal standard for the analysis. Nitrogen (Aga, 99.5%) was used for the pressurisation of the reactor.

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 the internal standard method. The identification of the products was performed with a gas chromatograph combined with a mass spectrometer (GC-MS) and the identification of the ether is discussed in detail in [7].

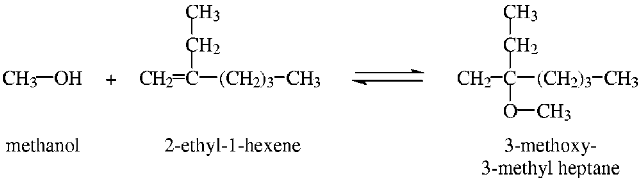
2.5. Calculation

Calculations were performed on molar basis. Conversions to products were calculated with respect to alkenes. The selectivity to the ether is defined here as the fraction of 2-ethyl-1-hexene consumed in the etherification relative to the total consumption of 2-ethyl-1-hexene. Accordingly, the selectivity to isomers is the ratio of the formed alkene isomers to the consumed 2-ethyl-1-hexene.

Contact time, i.e., time multiplied by the mass of dry catalyst, was used in the calculations to scale the results and eliminate the slight variations in the mass of catalyst in the various experiments. The activation energy was calculated from the initial rates according to Arrhenius' equation.

3. Results

The etherification of 2-ethyl-1-hexene (2E1H) with methanol was studied at 60–90 °C. The reaction scheme for the etherification is presented in scheme 1. The conversion of 2E1H to ether is presented in figure 1 as a function of the contact time at various temperatures. With stoichiometric feed an etherification conversion of 19% was achieved at 90 °C, while conversions of 23 and 26% were obtained at 80 and 70 °C, respectively. At 60 °C the reaction rate was too slow for the maximum etherification conversion to be reached within 28 h. The decreasing maximum conversion with increasing temperature (figure 1) indicates that the etherification reaction is exothermic and the shape of the conversion curve indicates that thermodynamic equilibrium is limiting the progress of the reaction. Exothermic reaction and the limiting role of the thermodynamic equilibrium are typical for this kind of etherification reactions [3].



Scheme 1. Reaction scheme for etherification of 2-ethyl-1-hexene with methanol to 3-methoxy-3-methylheptane.

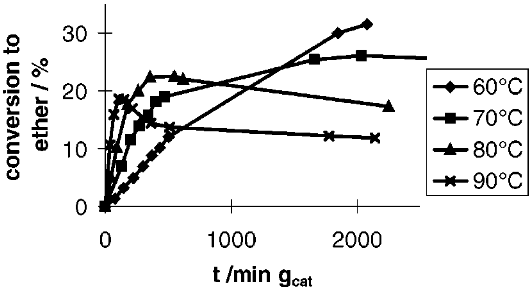


Figure 1. Etherification conversion of 2E1H at 60–90 °C.

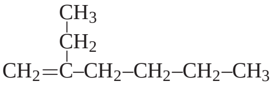
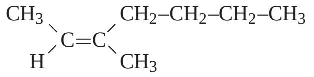
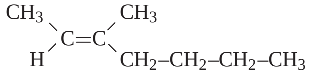
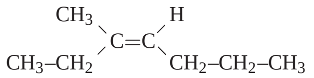
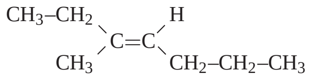
The activation energy for the ether formation was calculated from the initial rates according to the Arrhenius' equation. For the etherification experiments at 60–90 °C, an activation energy of 85 kJ/mol was obtained for the ether formation with linear regression ($R^2 = 0.995$). This activation energy is of the same order of magnitude as the activation energies obtained for the etherification of C_5- and some other C_8-alkenes [6,11]. If the internal diffusion had been limiting the reaction, the value of the activation energy would have been clearly lower.

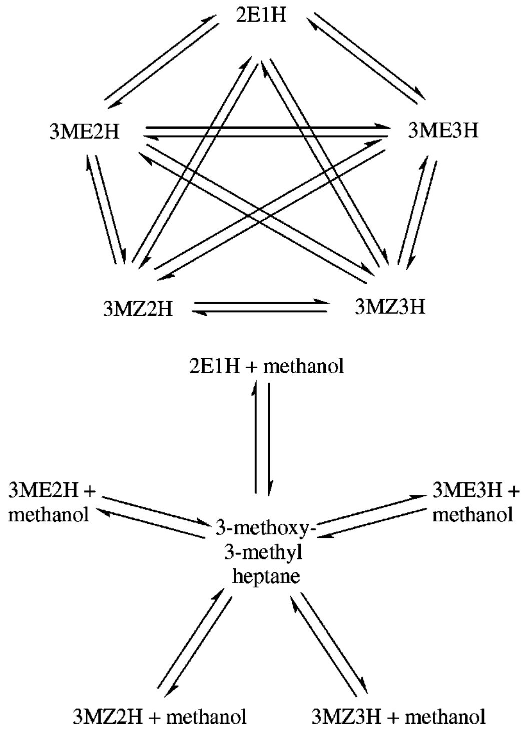
Double bond isomerisation of the alkenes was observed in addition to the etherification. The double bond of the alkene shifted from α-position to β-position, i.e., from the end of the carbon chain to the other side of the tertiary carbon atom, and four new alkene isomers were formed: 3-methyl-(Z)-2-heptene (3MZ2H), 3-methyl-(E)-2-heptene (3ME2H), 3-methyl-(Z)-3-heptene (3MZ3H) and 3-methyl-(E)-3-heptene (3ME3H). The five alkene isomers are presented in table 1. The attachment of the double bond of the alkene to a tertiary carbon atom indicates that all these isomers can react to ether under the mild conditions studied [12]. All the isomers are etherified to the same compound, 3-methoxy-3-methylheptane. The reaction rate of the etherification is faster when the double bond is in the α-position [12], and thus 2E1H, as the only α-alkene, is assumed to be the most reactive of the four isomers. The reaction network of etherification and isomerisation of the five isomers is presented in scheme 2.

The etherification and isomerisation reactions consumed 2E1H almost completely. At 70, 80 and 90 °C the total 2E1H conversion stabilised to a value of about 98%, but at 60 °C the maximum total conversion was not reached. The high total conversion indicates that the fraction of 2E1H is extremely small in equilibrium. As an example of a typical experiment, figure 2 presents the formation of the products as a function of contact time at 80 °C.

At 80 °C the initial rate of etherification was 0.11 mmol/(min g_{cat}) and the initial rate of isomerisation 0.12 mmol/(min g_{cat}). At the studied temperature range isomerisation was the main reaction with stoichiometric feed. Figure 3 illustrates the progress of the selectivities to isomerisation and etherification at various temperatures as a function of contact time with stoichiometric feed. The initial selectivities presented in figure 4 are obtained by extrapolating

Table 1
Alkene isomers detected.

 $CH_2{=}C(CH_2CH_3){-}CH_2{-}CH_2{-}CH_2{-}CH_3$	2-ethyl-1-hexene (2E1H)
	3-methyl-(Z)-2-heptene (3MZ2H)
	3-methyl-(E)-2-heptene (3ME2H)
	3-methyl-(Z)-3-heptene (3MZ3H)
	3-methyl-(E)-3-heptene (3ME3H)



Scheme 2. Reaction networks of isomerisation and etherification of alkene isomers.

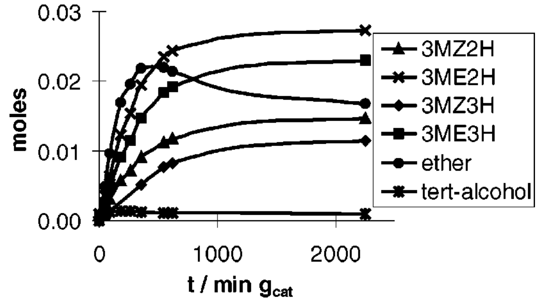


Figure 2. Amounts of product compounds as a function of contact time at 80 °C.

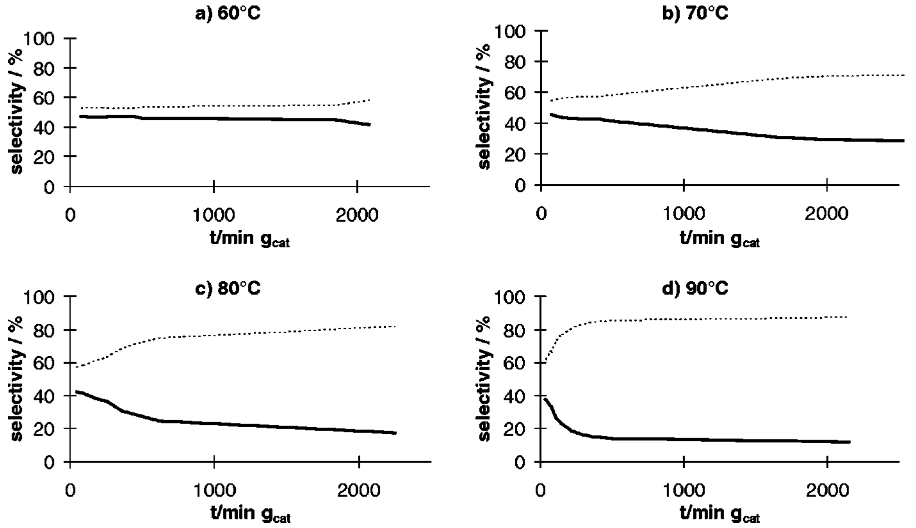


Figure 3. Selectivity to etherification and isomerisation at various temperatures. (—) Etherification, (- - -) isomerisation.

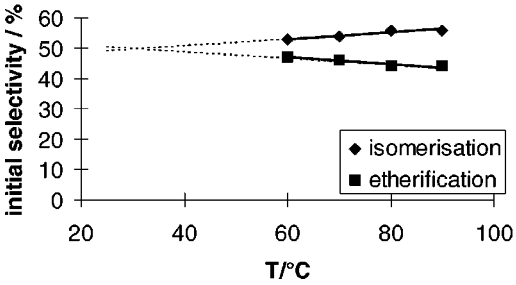


Figure 4. Initial selectivity to etherification and isomerisation as a function of reaction temperature.

Table 2
Molar fractions of isomers at 80 °C.

	Experimental	Thermodynamic
2-ethyl-1-hexene	0.023	0.016
3-methyl-(Z)-2-heptene	0.192	0.367
3-methyl-(E)-2-heptene	0.335	0.367
3-methyl-(Z)-3-heptene	0.156	0.125
3-methyl-(E)-3-heptene	0.293	0.125

these curves to the starting point (time = 0) of the reaction.

The isomerisation rate of the alkenes was 2.3 mmol/(min g_{cat}) without methanol in the feed: the initial consumption rate of 2E1H was over nine-fold that with equimolar methanol : alkene ratio and the isomerisation rate twenty times faster than in the presence of methanol. The isomerisation experiments were carried out long enough to bring the alkene isomers into steady state, i.e., to the point where the fractions of alkenes were stabilised. The composition at 80 °C is presented in the first column of table 2. A stationary composition for the alkenes was reached in approximately 1 h, and thereafter the oligomerisation of alkenes increased rapidly.

When the reaction took place without methanol a part of the alkenes became oligomerised. With methanol present in the feed, no formation of oligomer was detected in any experiment. Etherification of the alkene oligomers was neglected: the oligomers were considered as inert compounds since as bulky and large molecules their etherification is probably extremely slow. Indeed, the fraction of oligomers remained approximately constant throughout the etherification experiment and no new peaks indicating etherified oligomers appeared in the chromatogram. Quantitative analysis of oligomers was not possible with our procedure, however.

The equilibrium composition of the alkenes was calculated according to thermodynamic values of the alkene isomers as presented by Alberty and Gehrig [13]. Their values were determined for the gas phase, but since these compounds have not been studied in detail any more reliable liquid phase data were not available. In addition, since we are dealing with compounds that are very similar to one another, the gas phase data give a good estimate of the composition in the liquid phase too. The mole fractions of each of the five alkene isomers in the thermodynamic equilibrium mixture at 80 °C and 1 bar at gas phase are presented in the last column of table 2.

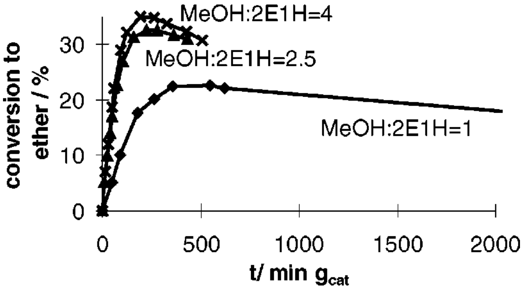


Figure 5. Etherification conversion of 2E1H as a function of contact time at various methanol : 2E1H ratios at 80 °C.

The stable composition of isomers obtained above was etherified further at 80 °C with a similar procedure to that used for pure 2E1H. The total etherification rate with the pre-isomerised mixture was 0.09 mmol/(min g_{cat}), i.e., 16% slower than the rate with pure 2E1H. The etherification rates of individual alkenes could not be compared because the alkene distribution remained constant and the individual isomerisations could not be distinguished.

The effect of methanol surplus on the ether formation was studied with initial methanol : 2E1H molar ratios of 1–4 with constant alkene concentration. Figure 5 presents the etherification conversion of 2E1H at each ratio at 80 °C, while figure 6 presents the selectivities to etherification and isomerisation for the same ratios, also at 80 °C. Figure 7 shows the initial rates for the formation of the ether and the isomerisation of 2E1H as a function of the methanol : 2E1H molar ratio.

4. Discussion

4.1. Etherification of 2E1H

The etherification conversion as a function of contact time is observed to pass through a maximum (figure 1). This overshooting can be explained in terms of the mutual equilibrium of the isomers in the reaction mixture.

At the beginning of the reaction, 2E1H and methanol were present in relatively large concentrations and their molar fractions were not limiting on the formation of ether. 2E1H, as an α-alkene, is presumed to be the most reactive isomer in the etherification reaction, analogously to the situation with other alkenes, like isoamylenes [12]. Simultaneously with the etherification, however, some isomerisation of 2E1H occurred and at some point after isomerisation had increased the molar fractions of the “new” alkene isomers in the mixture the equilibrium began to have an effect on the amount of ether. When 2E1H was in excess in the reaction mixture, the amount of ether became too great with respect to the equilibrium with the new alkene isomers, whose concentrations were gradually increasing. To establish equilibrium in the total reaction mixture, the ether began to decompose. This can be seen in figure 1 as the

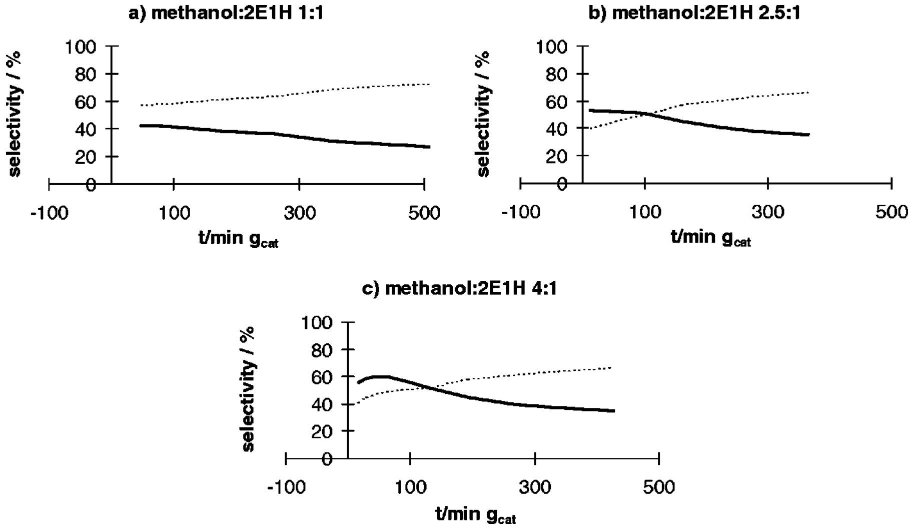


Figure 6. Selectivity to etherification and isomerisation at various methanol : 2E1H molar ratios at 80 °C. (—) Etherification, (- - -) isomerisation.

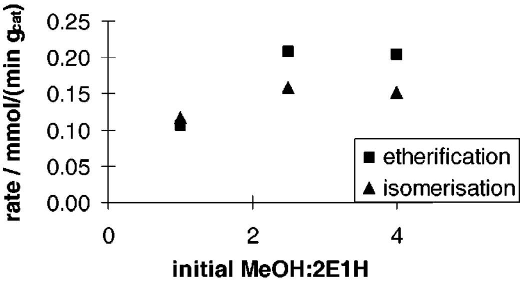


Figure 7. Initial rates of ether formation and isomerisation as a function of methanol : 2E1H ratios at 80 °C.

decrease in etherification conversion after the maximum. The decomposition of ether indicates that the equilibrium constant for the etherification of 2E1H is higher than the equilibrium constants for the etherification of other isomers. This is analogous to the behaviour of 2-methyl-1-butene in the production of TAME [14].

The situation in the reaction mixture is rather complex, as presented in scheme 2, since there are five equilibrium-limited etherification reactions taking place simultaneously, and the isomerisation reactions between the five alkene isomers are also equilibrium limited. Thus, in principle, fifteen equilibrium-limited reactions are occurring, or thirty individual reactions. Probably some of these reactions are so slow that they could be neglected in the reaction scheme, but our data does not allow us to decide which reactions could be ruled out.

The selectivity to etherification decreased significantly with increasing temperature, as seen in figure 3. Isomerisation was the dominant reaction in the studied temperature range. The difference between the selectivities to the ether and the alkene isomers was smallest at 60 °C, and increased with temperature. Extrapolation to lower temperature suggests that with stoichiometric feed the etherification would become the main reaction at about 30 °C (figure 4). The trend of decreasing selectivity to ether as a function of contact time depends on the extent of the reaction, i.e., etherification reaction is suppressed as the reaction proceeds because of the diminishing fractions of reactants and equilibrium limitations. At 60 °C the selectivity was more or less constant with time because both etherification and isomerisation reactions are then so slow that equilibrium restrictions are not encountered in the studied time scale.

4.2. Etherification of the isomerised C_8 mixture

To study the differences in reactivity of the various alkenes, we isomerised 2E1H to stationary composition before adding methanol to accomplish the etherification. Unlike the conversion of pure 2E1H (figure 1), the conversion of the isomerised mixture did not pass through a maximum. In the case of the isomerised mixture, and in contrast to the pure 2E1H, the equilibrium between the alkene isomers had been established before the etherification commenced and no large deviations from this equilibrium occurred during etherification.

The etherification rate was lower with the pre-isomerised alkene mixture than with 2E1H. The lower rate was due to the different reaction mixtures: as an α-alkene, 2E1H can be presumed to be highly reactive [12], whereas the fraction of the less reactive isomers probably dominates in the pre-isomerised mixture. In both experiments the conversion to the ether stabilised to the same level, which presumably is determined by thermodynamic equilibrium.

Most probably the etherification did not consume all the isomers in the same proportion, but the fractions of the isomers nevertheless continued constant through the experiment because isomerisation quickly re-established the alkene distribution. The rate of isomerisation cannot be determined from our results, however, as this would require knowledge of the reaction rate of each isomer.

Both the experiments and the calculated thermodynamic results show the almost complete conversion of 2E1H to other isomers. As seen in table 2, the composition of our isomer mixture is close to that of the thermodynamic mixture in gas phase [13]. The largest differences between the experimental and thermodynamic values are for 3MZ2H and 3ME3H. Note, however, that thermodynamic values are the same for 3MZ2H and 3ME2H and for 3MZ3H and 3ME3H. Although this is a highly unlikely result, it is also understandable. The thermodynamic values are based on theoretical estimations and the estimations evidently do not distinguish between the geometric isomers. Our experimental determination of the composition would seem, therefore, to be the more reliable approach for determining the thermodynamic equilibrium of the alkenes.

In the case of some previously studied isomer pairs of other alkenes (e.g., C_5s [15], C_6s [16] and C_8s [6]), the reactivity of the two isomers was inversely proportional to their fraction in the thermodynamic mixture. The same situation was found for a system of three alkene isomers [17]: in the network of 2-ethyl-1-butene, *trans*-3-methyl-2-pentene and *cis*-3-methyl-2-pentene the reactivity decreased in the listed direction and the molar fractions at equilibrium in the reverse direction. If our system of five isomers obeys the same relation, 2E1H which appeared as the smallest fraction should be the most reactive isomer in etherification and the reactivity should decrease in the order 2E1H $>$ 3MZ3H $>$ 3MZ2H $>$ 3ME3H $>$ 3ME2H. This is the experimental order indicated both in figure 2 and in table 2.

Isomerisation of the alkenes disturbs the etherification, even though the isomerised products are also capable of being etherified. As seen in the differences between the initial rates, the problem is that some isomers are less reactive in etherification. Furthermore, if the etherification and isomerisation reactions proceed via the same intermediates, the isomerisation would unnecessarily consume active intermediate compounds that otherwise would be etherified directly. Thus, suppression of isomerisation could be beneficial for a higher ether yield and was therefore studied further.

4.3. Effect of methanol surplus

The finding of a larger amount of ether in the early stage of the reaction than at the equilibrium state (see figure 1) suggested a study of the conditions providing maximum ether yield. In other words, conditions suppressing the isomerisation of 2E1H were sought.

Owing to its polarity, methanol easily adsorbs on the catalyst, and thus excess of methanol could be assumed to inhibit the isomerisation by hindering the adsorption of alkene molecules on the catalyst. Indeed, as seen in figures 5 and 7, surplus of methanol does appear to enhance the ether formation, and the etherification rate increases noticeably with increase in the initial methanol : 2E1H ratio. The methanol : 2E1H ratio has considerably less effect on the isomerisation so that selectivity to ether is enhanced (figure 6). Thus more of the valuable alkene feed stock is utilised in the etherification reaction when operating with methanol surplus. Taking into account the results obtained with the stoichiometric feed in figure 3, we can conclude that the selectivity towards etherification is enhanced by lowering the temperature and increasing the methanol : 2E1H molar ratio.

When there is a surplus of one of the reagents, thermodynamic factors force the other reagent to react more completely. In our case the conversion of alkene is enhanced by the surplus of methanol. The thermodynamics does not, however, explain the selectivity effects in figure 6. The overshooting of the etherification conversion (figure 5) leads to the production of more ether than in principle is possible: if the reaction is stopped when the conversion is at maximum, the yield of ether is higher than the theoretical value.

In addition to improved selectivity to ether, also the reaction rate was affected by the methanol : 2E1H molar ratio. A drastic difference in the reaction rate was observed when the ratio was increased from 0 to 1: the total consumption rate of 2E1H decreased by 87%. This result was predictable, since methanol is known to inhibit the reactivity of alkenes [6,18]. A good example of the inhibiting effect of methanol on the reaction rate is provided by the isomerisation of 2E1H: without methanol the equilibrium among the isomers was established in 1 h, whereas with equimolar feed of methanol and alkene the equilibrium between the alkenes was reached only after a few days.

The methanol concentration of the reaction mixture affects the activity of the catalyst [19]. At lower concentration of methanol the active sites on the catalyst are polymer-bound $-SO_3H$ groups, which are highly active. As the methanol concentration increases, methanol starts to dissociate the acid groups, and solvated protons, which are less active, become the active sites. Further increase in the methanol concentration does not affect the reaction rate. We observed high catalyst activity at very low methanol concentrations (ratio of methanol to 2E1H approximately 0), and decrease in the activity with increasing methanol concentration up to methanol : 2E1H ratio of 1. Thereafter, however, the activity started to increase (see figure 7). This increase with methanol : 2E1H ratio suggests that the excess of methanol helps to activate the alkene towards reaction and promotes its reactivity. In most instances of etherification, the reaction rate is reported to decrease with increasing methanol fraction and finally to become independent of it above a particular alcohol fraction [20–23].

Although favourable for the selectivity towards etherification, the drawback of excess methanol is the risk for increasing formation of dimethyl ether, especially at higher temperatures [24]. The conversion of methanol to dimethyl ether was observed to be slightly higher with excess methanol than at equimolar ratio, but since the conversion was less than 0.3% in a one-day experiment, the formation is of minor importance in our system. Owing to its small fraction, dimethyl ether is not included in figure 2.

4.4. Side reactions

The side reactions, i.e., other reactions besides etherification and isomerisation of alkenes, were minor and thus the selectivities to ether and isomers presented in figures 3 and 6 sum to almost 100%. Conversion to by-products, mainly dimethyl ether and 3-methyl-3-heptanol, was less than 1% in individual experiments. Dimethyl ether is formed from methanol in a dehydration reaction and 3-methyl-3-heptanol from alkene and water in a hydration reaction. The hydration of alkenes is generally considered to take place more rapidly than etherification because water is more polar than methanol, and by easily attaching to the catalyst surface it also reacts first [25,26]. As observed here (figure 2), the available water reacted to tertiary alcohol at an early stage relative to the other reactions. The formation of tertiary alcohol declined after the first hour, and the amount of 3-methyl-3-heptanol in the reaction mixture remained constant thereafter. Hydration of alkenes is an equilibrium-limited reaction, and the amount of water served to limit the formation. Even though the catalyst is pre-treated, some water will remain, mainly tightly trapped in the pores of the ion exchange resin because water forms strong hydrogen bonds with the sulfonic acid groups on the catalyst surface [19].

5. Conclusions

The etherification reaction of 2-ethyl-1-hexene with methanol was studied. In addition to etherification, isomerisation of 2-ethyl-1-hexene was observed, and four new alkene isomers were detected. In reaction with methanol, all five alkenes produced 3-methoxy-3-methyl heptane.

The thermodynamic mixture of alkenes reacted more slowly than pure 2-ethyl-1-hexene, which means that isomerisation of the alkenes retards etherification. Evidently the isomers have different reactivity and different equilibrium in the etherification, most probably due to their different structures: 2E1H is the only α-isomer. To maximise the formation of ether, the reaction should be performed at low temperatures where the selectivity to the ether is higher, and the position of the conversion maximum should be carefully determined. The yield of ether can also be improved by operating with methanol surplus.

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References

[1] Executive order D-5-99 by the Governor of the State of California (25 March 1999).

[2] California Energy Commission, Supply and cost of alternatives to MTBE in gasoline, Publication No. P300-98-013 (1998).

[3] J. Kivi, O. Krause and L. Rihko, Kem. Kemi 18 (1991) 356.

[4] W.J. Piel, Fuel Reformulation 4 (2) (1994) 28.

[5] J. Kivi, A. Rautiola, J. Kokko, J. Pentikäinen, P. Aakko, M. Kytö and M. Lappi, SAE paper 971724 (1997).

[6] R.S. Karinen and A.O.I. Krause, Appl. Catal. A 188 (1999) 249.

[7] R.S. Karinen, A.O.I. Krause, E.Y.O. Tikkanen and T.T. Pakkanen, J. Mol. Catal. A 152 (2000) 253.

[8] F. Cunill, M. Vila, J.F. Izquierdo, M. Iborra and J. Tejero, Ind. Eng. Chem. Res. 32 (1993) 564.

[9] J.A. Linnekoski, A.O.I. Krause and L.K. Struckmann, Appl. Catal. A 170 (1998) 117.

[10] E. Tikkanen and T.T. Pakkanen, manuscript.

[11] J.A. Linnekoski, A.O.I. Krause and L.K. Rihko, Ind. Eng. Chem. Res. 36 (1997) 310.

[12] A.O.I. Krause and L.G. Hammarström, Appl. Catal. 30 (1987) 313.

[13] R.A. Alberty and C.A. Gehrig, J. Phys. Chem. Ref. Data 14 (1985) 803.

[14] L.K. Rihko, J.A. Linnekoski and A.O.I. Krause, J. Chem. Eng. Data 39 (1994) 700.

[15] L.K. Rihko, P.K. Kiviranta-Pääkkönen and A.O.I. Krause, Ind. Eng. Chem. Res. 36 (1997) 614.

[16] T. Zhang and R. Datta, Ind. Eng. Chem. Res. 34 (1995) 2247.

[17] T. Zhang and R. Datta, Chem. Eng. Sci. 51 (1996) 649.

[18] J.F. Izquierdo, M. Vila, J. Tejero, F. Cunill and M. Iborra, Appl. Catal. A 106 (1993) 155.

[19] A. Chakrabarti and M.M. Sharma, React. Polym. 20 (1993) 1.

[20] J.A. Linnekoski, P. Kiviranta-Pääkkönen, A.O.I. Krause and L.K. Rihko-Struckmann, Ind. Eng. Chem. Res. 38 (1999) 4563.

[21] F. Ancillotti, M. Mauri and E. Pescarollo, J. Catal. 46 (1977) 49.

[22] J.A. Linnekoski, A.O.I. Krause, A. Holmen, M. Kjetså and K. Moljord, Appl. Catal. A 174 (1998) 1.

[23] N.S. Caetano, J.M. Loureiro and A.E. Rodrigues, Chem. Eng. Sci. 49 (1994) 4589.

[24] P.K. Kiviranta-Pääkkönen, L.K. Struckmann, J.A. Linnekoski and A.O.I. Krause, Ind. Eng. Chem. Res. 37 (1998) 18.

[25] S.S. Jayadeokar and M.M. Sharma, React. Polym. 19 (1993) 169.

[26] J. Tejero, A. Calderón, F. Cunill, J.F. Izquierdo and M. Iborra, React. Funct. Polym. 33 (1997) 201.