Journal of Catalysis 262 (2009) 18–26

Contents lists available at ScienceDirect

Journal of Catalysis

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Polarity of the acid chain of esters and transesterification activity of acid catalysts

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ARTICLE INFO

Article history:
Received 1 October 2008
Accepted 21 November 2008
Available online 7 January 2009

Keywords:
Esterification
Transesterification
Acid catalyst
Biodiesel
Reichardt's dye
$E_T(30)$ polarity scale

ABSTRACT

The effect of polarity of the esters on the transesterification reaction rate has been investigated. The effect was studied in homogeneous and heterogeneous catalysts. The polarity of different ethyl alkanoate esters was varied by (i) increasing the number of carbon atoms in the acid alkyl chain of the esters and (ii) introducing Br and hydroxy substituents at the end of the acid chain of ethyl hexanoate. Polarity was determined through the λ_{max} of the UV–Vis spectrum of the betaine dye dissolved in the investigated esters ($E_T(30)$ scale). The transesterification reaction was carried out with methanol and by using sulfuric acid and a Dowex DR2030 sulfonic resin as homogeneous and heterogeneous catalysts, respectively. It was observed that, in addition to steric hindrance, the polarity of the ester chain has an effect on the reaction rate of the heterogeneous acid catalysts. It is proposed that the positive or negative effect of the polarity is due to repulsive or attractive interactions of the ester chain with the polar groups of the resin and/or with the methanol molecules present in the pores. A very positive effect is found in heterogeneous acid catalysis if H-bonds can stabilize the active intermediate participating in the rate determining step. The attractive or repulsive interactions are absent in the homogeneous case.

1. Introduction

Esterification and transesterification reactions are widely used for the synthesis of fine chemicals [1], pharmaceuticals [2], plastics monomers [3], and many other chemical products [4]. Nowadays, interest in these reactions has increased because they are required for the production of biodiesel, a mixture of fatty acid methyl esters (FAME). Biodiesel is a non-toxic biodegradable fuel produced from vegetable oils, and is now widely accepted as environmental friendly and as a renewable fuel provided by biomass [5,6].

Many processes using esterification and transesterification reactions are carried out by using homogeneous acid catalysts. The use of homogeneous acid catalysts has serious drawbacks: they are corrosive and they must be neutralized at the end of the reaction; they cannot be recovered, generating wastewaters and increasing the cost of the overall process. To cope with the problems associated with homogeneous processes, solid acid catalysts have been proposed. However homogeneous reactions always proceed at higher rates than when heterogeneous catalysts are used. Moreover when heterogeneous esterification and transesterification reactions are applied to carboxylic acids and esters with short fatty acid chains, both reactions proceed at reaction rates that are still satisfactory. By contrast, when applied to long chain or more voluminous carboxylic acids or esters, the heterogeneous reactions proceed at much slower reaction rates and longer reaction times, and higher temperatures are required to achieve conversions comparable to those of homogeneous catalysts [7–9]. An explanation is required for these effects.

In principle, one can assign the lower activity in solid catalysts to mass transfer restrictions derived from the lower diffusion coefficient of heavier molecules and/or from the porous character of solid catalysts. However, in the case of esterification of carboxylic acids by homogeneous catalysis there are no mass transfer restrictions, and low reaction rates are also found for longer acid chains. In such cases, steric effects related with the size of the molecule and with preferential conformations have been invoked to explain the lower reaction rate of the esterification of carboxylic acid with longer chains [7].

The esterification reaction catalyzed by homogeneous acids proceeds through the following mechanism: in a first step, the carbonyl oxygen is attacked by the acid proton that increases the electrophilicity of the carbon atom. This carbon atom is then more susceptible to the nucleophilic attack of the hydroxyl group of the alcohol, which is the rate determining step. The following steps are the dehydration and deprotonation (esterification) of the intermediate with the corresponding formation of the new ester and the recovery of the catalyst [10,11]. Taking into account that transesterification proceeds through a similar mechanism (see Scheme 1), the same steric and conformational effects can be invoked to explain the lower activity found in the transesterification of esters

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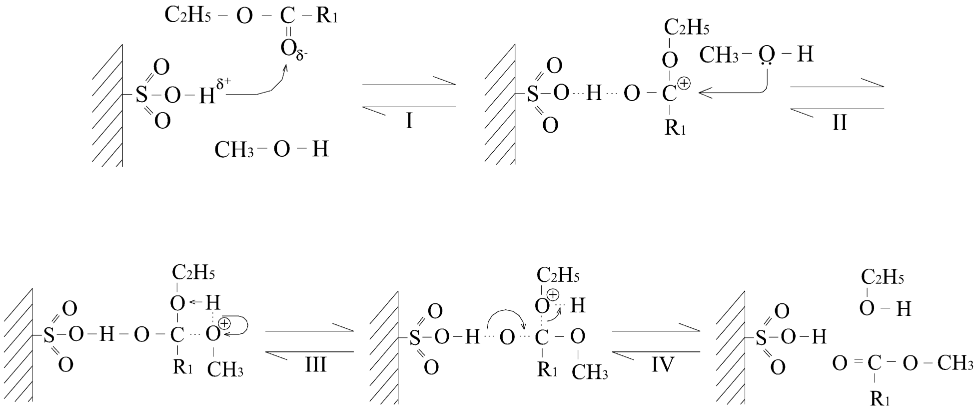
doi:10.1016/j.jcat.2008.11.026



Scheme 1.

with longer or more voluminous acid chain by using homogeneous acid catalysts. In the case of heterogeneous catalysts similar effects can explain the lower activity, albeit enhanced by their solid nature [7].

Less attention has been paid to the polar character of the acid chain. The aim of this article is to understand the role of the polarity of the acid chain of esters on the transesterification reaction rate when using homogeneous and, especially, heterogeneous acid catalysts. In this work, the reaction rate of the methanolysis of different ethyl esters using a sulfonic resin was determined and was compared with those obtained with sulfuric acid as homogeneous catalyst. The alkyl chain of the carboxylic fragment was varied (i) by increasing the number of carbon atoms and (ii) by introducing polar functionalities at the opposite end of the acid chain in esters with the same number of carbon atoms. The first strategy accounts for steric effects as well as for polarity effects, but the second series should account only for polarity effects.

It will be shown that, when using heterogeneous acid catalysts, the transesterification reaction rate can be largely improved by increasing the polarity of the chain of the acid group in the ester (an ester group has two moieties, the acid group and the alcohol group), especially when functionalities in the acid chain allow for the formation of hydrogen bonds between the acid chain and the surface of the catalysts and/or with liquid methanol molecules present within the pores of catalyst. In the case of homogeneous catalyst, the effect of polarity is negligible. The conclusions presented here can be extended to esterification reactions.

The polarity of a given molecule is defined through its solvation capacity, that is, “through its capacity to establish non-specific and specific intermolecular interactions with a given solute, excluding obviously those interactions leading to chemical alterations of the solute (such as protonation, oxidation, reduction, complex formation, etc.)” [12,13]. The non-specific interactions include purely electrostatic forces arising from Coulomb interactions and polarization forces (those between ion and non-polar molecule, dipolar/non-dipolar molecule and two non-polar molecules). The specific forces include hydrogen bond between hydrogen bond donating (HBD) and accepting (HBA) molecules and the interactions between electron pair donor (EPD) and electron pair acceptor (EPA) molecules.

Among the various methodologies that can be used for the measurement of polarity, solvatochromic effect has been selected for this article. Solvatochromism is the change in the position, intensity and shape of UV/Vis/near IR absorption spectra of a chemical probe when dissolved in the molecule whose polarity is to be determined [12,13]. Specifically, the widely applied and well-established Dimroth–Reichardt $E_T(30)$ scale will be used. This scale is based on the changes in the position of the intramolecular charge transfer (CT) of the π–π^* absorption band of the pyridinium *N*-phenolate betaine dye (Reichardt's dye) [12,13]. The details of the experimental procedure will be presented in the experimental section. Basically, it involves measuring the wavelength of the CT band when the dye is dissolved in the different esters studied in this work, and the $E_T(30)$ magnitude will be determined from the wavelength. The data of $E_T(30)$ for a number of molecules is tabulated in Refs. [12,13] that facilitates the comparison with the molecules studied in this work.

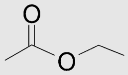
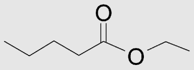
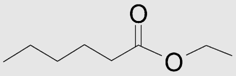
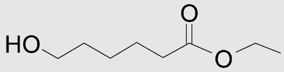
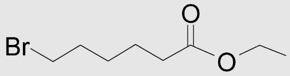
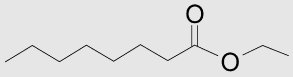
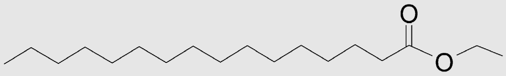
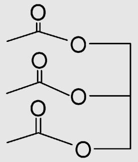
The choice of this methodology tacitly assumes that the interactions established between Reichardt's probe and the esters are of the same type as those established between the ester and both the polymeric chains of the sulfonic resins and the methanol molecule. The band position of Reichardt's dye is very sensitive to HBD–HBA properties and to non-specific interactions with the solvents (the esters), whereas its sensitivity to interactions like EPD or EPA is negligible [12,13]. We assume that the former type of interactions between the acid chain of the ester and both the polymeric chain and methanol molecule are essential in explaining the effect of polarity on the transesterification rate, whereas the latter properties are irrelevant. Therefore, $E_T(30)$ appears as a very suitable scale for our purpose. It will be shown that structural changes in the sulfonic resin (unfolding, swelling, etc.) driven by the different polarity of the esters are minimal in the selected resin, and therefore the contribution of these changes to the reaction rate are also negligible. Negative or positive inductive effects of the polar group transmitted through the hydrocarbon chain to the ester group can be considered negligible because of the long distance between them. The non-specific and hydrogen bond properties of the esters may be affected because of their presence within the nanocavities of the solid, although these variations are expected to be similar in all the investigated esters.

2. Experimental

2.1. *Description of the catalytic resin*

All the catalytic experiments were carried out using a Dowex DR2030 ion exchange resin in its dried form supplied by Dowex as 1.19–0.42 mm beads (moisture content is less than 3%, mesh size 16–40). The Dowex DR2030 catalyst is based on divinylbenzene (DVB) and styrene copolymer and functionalized with sulfonic acid groups (weight capacity >4.7 meq $H^+ g^{-1}$). This polymer was chosen because of its mesoporosity and relatively large pore volume (0.33 $cm^3 g^{-1}$). The specific surface was determined using a Micromeritics ASAP 2000 apparatus to record the N_2 adsorption isotherm at 77 K after evacuation at 363 K for 20 h and applying the BET method. The value was 29.8 ± 0.2 $m^2 g^{-1}$ – consistent with that given by the supplier. The mean pore diameter obtained by applying the BJH method to the desorption isotherm

Table 1
Ethyl esters investigated in this work.

Name	Molecular structure	No. of carbon atoms in the acid chain of the ester
Ethyl acetate		2
Ethyl pentanoate (or valerate)		5
Ethyl hexanoate (caproate)		6
Ethyl 6-hydroxyhexanoate		6
Ethyl 6-bromohexanoate		6
Ethyl octanoate (or caprylate)		8
Ethyl hexadecanoate (or palmitate)		16
Glyceryl triacetate		2[a]

[a] It is not an ethyl ester.

was between 40 and 50 nm. The sulfonic loading was determined by titration with NaOH solution and by using phenolphthalein as indicator, and was found to be 4.7 meq $H^+ g^{-1}$.

2.2. Investigated ethyl esters

Table 1 presents the ethyl esters studied in this work. The variation in the polarity of the acid chain of the esters was achieved by two means. In a first series, the polarity changes by increasing the length of the carboxylic alkyl chain. Thus, ethyl acetate (Sigma-Aldrich, purity >99%) ethyl pentanoate (Sigma-Aldrich, purity >99%), ethyl hexanoate (Alfa Aesar, purity >99%), ethyl octanoate (Sigma-Aldrich, purity >99%) and ethyl hexadecanoate (Fluka, purity >95%) esters were selected. Table 1 also indicates common names used for ethyl pentanoate, hexanoate, octanoate and hexadecanoate. In a second series, the polarity of the ethyl hexanoate ester is modified by introducing a hydroxyl or bromo group at the opposite end of the carboxylic group. Thus ethyl 6-hydroxyhexanoate (Sigma-Aldrich, purity >98%) and ethyl 6-bromohexanoate (Alfa Aesar, purity >98%) esters were used. Besides these two series, glyceryl triacetate (Sigma-Aldrich, purity >99%) was also included in the study as a model of short chain triglyceride. In principle and if it is not mentioned all these esters were investigated in reaction as received, with no further purification.

2.3. Catalytic activity measurements

The transesterification of the esters was carried out in a 125 mL three-necked jacketed glass reactor. A reflux condenser was connected to one of the necks and a dropping funnel was connected to another. In all cases, 114 mmol of ester was placed in contact with the catalyst. In the case of the sulfonic resin, 2 g of solid was added to the ester, that is, 9.4 meq H^+. The resin was ground to obtain finer particles with diameter $\varnothing < 0.106$ mm. The temperature of the ester–catalyst mixture was set to 333 K by circulating water through the jacket of the reactor with a re-circulating bath. The mixture was under vigorous shaking (1000 rpm). The transesterification reaction started when methanol (0.005% H_2O Riedel de Häen) preheated to 333 K was added to the mixture through the dropping funnel. The methanol/ester molar ratio was 2:1. The reaction was carried out at atmospheric pressure for 3 h in the case of the solid resin. Aliquots at different reaction times were taken and the reaction was ended by rapidly cooling down to room temperature. The solid catalyst is then easily separated from the liquids by filtering.

In the case of the homogeneous catalyst, a much smaller amount of sulfuric acid was used and the reaction time was shorter (1 h) in order to achieve conversions comparable to that of the sulfonic resin. The same amount of ester was used (114 mmol) and then heated to 333 K, whereupon a sulfuric acid methanolic solution at 333 K was added so as to achieve the methanol/ester molar ratio 2:1. The methanol incorporates the sulfuric acid amounting to 58.4 mg of sulfuric acid, that is, 0.6 meq H^+. The analysis of the compositions was carried out immediately to prevent the progress of the reaction.

The liquid aliquots were analyzed in an Agilent 6890 GC equipped with a HP INNOwax capillary column (30 m × 320 μm × 0.50 μm). An aliquot of 250 mg of the liquid sample was added to 5 mL of acetone. Since the carbon balance was always >95%, the yield corresponds basically to the conversion of the ethyl ester. The yield to methyl ester was calculated from the relative areas of the methyl and ethyl esters using the equations

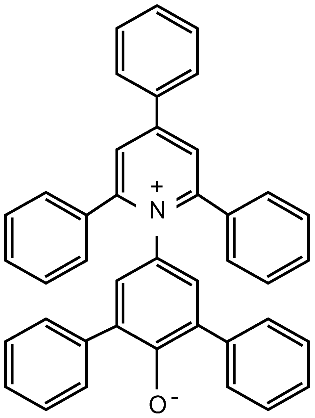


Fig. 1. Molecular structure of Reichardt's dye.

$$\text{Yield (\%)} = \frac{\text{mol methylester}}{\text{mol initial ethylester}} \times 100 = \frac{\frac{\text{mol methylester}}{\text{mol ethylester}}}{1 + \frac{\text{mol methylester}}{\text{mol ethylester}}} \times 100, \qquad (1)$$

where

$$\frac{\text{mol methylester}}{\text{mol ethylester}} = \frac{\frac{\text{area methylester}}{\text{MW methylester}}}{\frac{\text{area ethylester}}{\text{MW ethylester}}}. \qquad (2)$$

It is assumed that the chromatographic factors for methyl and ethyl esters are similar and that no other products in addition to methyl ester can be formed. Only in the case of the ethyl 6-hydroxyhexanoate were other products formed, as will be discussed later. The error in the determination of the yield was ±5% of the absolute yield value.

2.4. $E_T(30)$ values obtained by UV/Vis spectroscopy measurements of Reichardt's dye

The UV/Vis maxima of the absorption bands of Reichardt's dye (2,6-diphenyl-4-(2,4,6-triphenylpyridinio) phenolate, Aldrich 90%), also known as betaine dye, in each ester were recorded in a Varian (Cary E1) double-beam spectrophotometer to correct ester absorption on-line. Fig. 1 represents the chemical structure of the betaine. A few milligrams of Reichardt's dye were dissolved in each ester and the spectrum was collected at ambient temperature from 300 to 900 nm with a resolution of 1 nm using a quartz cell of 1 cm thickness. The esters were dried for two days with a molecular sieve in order to remove any water present.

$E_T(30)$ values is the energy of the electronic transition of the intramolecular charge transfer (CT) of the π–π^* absorption band of Reichardt's dye expressed in $\text{kcal}\,\text{mol}^{-1}$ when measured at room temperature (298 K) and atmospheric pressure. Once the $\lambda_{\max}$ (maximum of the band) is determined (the error was always smaller than ±2 nm), $E_T(30)$ was calculated as follows [12]:

$$E_T(30)\left(\frac{\text{kcal}}{\text{mol}}\right) = \frac{28591}{\lambda_{\max}\ (\text{nm})}. \qquad (3)$$

3. Results

3.1. Polarity of the esters

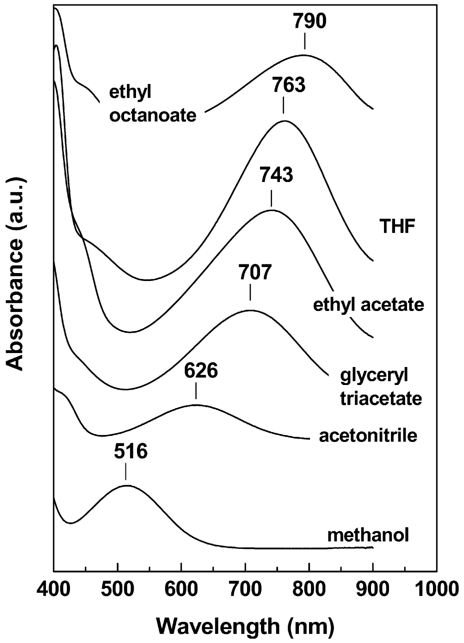


Fig. 2. UV–Vis spectra of betaine dye in some common solvents and in glyceryl triacetate, ethyl acetate and ethyl octanoate in the region of interest.

Table 2
$\lambda_{\max}$ and $E_T(30)$ of some solvents and of the different esters investigated.

Solvent	Wavenumber (nm)	$E_T[30]$ (kcal/mol)
THF	763	37.5 (37.4)[a]
Acetonitrile	626	45.7 (45.6)[a]
MeOH	517	55.3 (55.4)[a]
Ethyl acetate	743	38.5 (38.1)[a]
Ethyl pentanoate	779	36.7
Ethyl hexanoate	780	36.6
Ethyl 6-hydroxyhexanoate	570	50.2
Ethyl 6-bromohexanoate	627	45.6
Ethyl octanoate	790	36.2
Ethyl hexadecanoate	–	35.9[b]
Glyceryl triacetate	707	40.4 (40.1)[a]

[a] Values in parentheses are those tabulated in [12,14].
[b] Estimated value (see text for explanation).

Fig. 2 shows the region of interest of the UV–Vis spectra of betaine dye in some common solvents (methanol included) and some of the esters investigated in this work. The betaine dye is a negative solvatochromic compound, and then the CT π–π^* bands in more polar molecules are blue shifted (lower wavelength). The ground state of dye is more stabilized by solvation with polar molecules than the excited state, and then the energy difference increases [12]. Among the different molecules presented in the figure, the betaine band peaks at the lowest wavelength when dissolved in methanol and in methyl octanoate at the longest wavelength. The molecules represented in the figure can be ordered according to their betaine $\lambda_{\max}$ as follows:

$$\text{methanol} < \text{acetonitrile} < \text{glyceryl triacetate} < \text{ethyl acetate} < \text{THF} < \text{ethyl octanoate}.$$

This order is a consequence of the strength of solvation of Reichardt's dye by the molecules and therefore of their polarity. It is worth noting that glyceryl triacetate is more polar than ethyl acetate and the latter more polar than ethyl octanoate.

Table 2 summarizes the $\lambda_{\max}$ and $E_T(30)$ values of the dye when dissolved in the investigated molecules. For some of the molecules tabulated (THF, acetonitrile, methanol, ethyl acetate and glyceryl triacetate), the well-accepted values reported in the literature [12,14] are also included between brackets in the $E_T(30)$ column. The values determined experimentally are in good agreement with reported $E_T(30)$ values. In Fig. 3, the experimentally

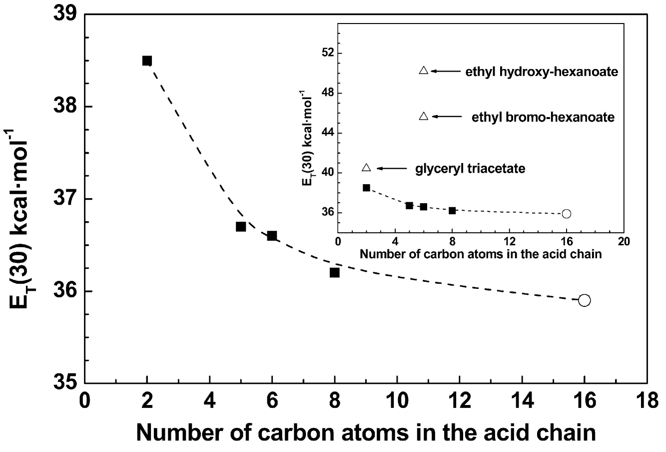
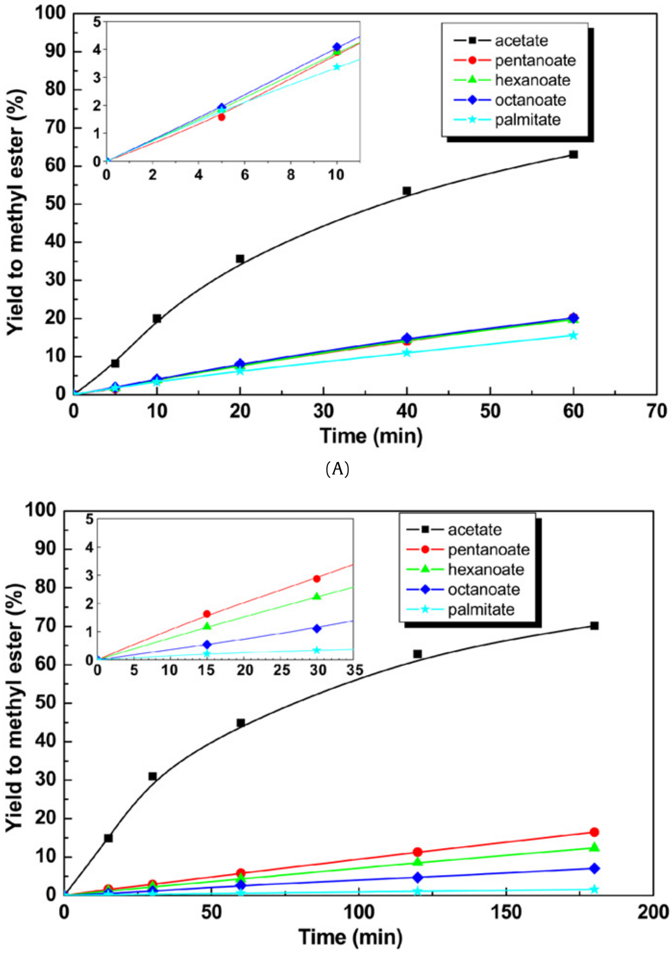


Fig. 3. $E_T(30)$ values vs. number of carbon atoms of the investigated esters: (■) non-substituted linear carboxylate esters; (○) extrapolation value for ethyl hexadecanoate and (△) bromo- or hydroxyethyl hexanoate and glyceryl triacetate.

determined $E_T(30)$ values are represented vs. the number of carbon atoms of the acid chain in the ester: in the main figure, the values for the alkyl chain, without polar groups, are represented by the ■ symbols, whereas in the inset of Fig. 3 the values for the OH and Br-substituted ethyl hexanoate and for the glyceryl triacetate are represented by the △ symbols. The value for hexadecanoate could not be determined because Reichardt's dye is not soluble in it. An estimation (○) was proposed according to the well-established behavior for other series, such as linear 1-alkyl alcohols. In the latter series, the $E_T(30)$ value decreases in a non-linear mode with the increase of the chain length, and reaches an asymptotic value for the alcohols with 10–11 carbon atoms. A further increase in the chain length does not result in a lower $E_T(30)$ value [12]. A similar trend is expected for the ethyl alkanoate esters, whereby a good approximation for the $E_T(30)$ of ethyl hexadecanoate can be 35.8–36.0 kcal mol^{-1} (35.9 was tabulated). The value of the latter is only 2.6 kcal mol^{-1} smaller than that of the ethyl acetate. Larger differences are found for the Br and OH substituted esters: $E_T(30)$ for the Br ethyl hexanoate is 9 kcal mol^{-1} larger than that of its non-substituted equivalent and this difference is even larger for the hydroxyl substituted ester (13.6 kcal mol^{-1} larger). $E_T(30)$ values of glyceryl triacetate is ca. 2 kcal mol^{-1} larger than that of ethyl acetate

The UV–Vis spectrum of betaine dye is very sensitive to non-specific forces and to the HBD–HBA forces, whereas it is rather insensitive to EPD–EPA interactions. In the non-substituted ethyl alkanoate series, the asymptotic trend can be explained as follows: the ester group would contribute to the same extent to the solvation energy, and the only variations are expected from the non-specific forces of the acid chain. The introduction of non-polar $-CH_2-$ units results in an increasingly larger contribution from the non-specific forces that are less intense. As a result, the polarity of the molecule decreases and so do the $E_T(30)$ values. The distant $-CH_2-$ units have no effect on the probe molecule, and the effect of the non-specific forces becomes constant as the alkyl chain becomes larger than 10–11 carbon atoms.

The presence of a Br group at the end of the hexanoate chain means that stronger non-specific interactions can be established between this molecule and Reichardt's dye since, as is well-reported, the Br group brings in stronger non-specific type forces (polarity/polarizability) that are superimposed onto those of the $-CH_2-$ units with less capacity to shift the λ_{max} [12,14]. This is reflected in a large $E_T(30)$ value of the ethyl bromohexanoate with respect to that of ethyl hexanoate. In contrast, the presence of a hydroxyl (OH) group involves a HBD–HBA type interaction with the betaine dye. These types of interactions have proven to be stronger than those caused by the $-CH_2-$ units or Br group and therefore result in larger increases in the $E_T(30)$ [12,14]. It is well known that the OH group increases polarity when present in any molecule.



(A)

(B)

Fig. 4. Yield to methyl ester for the non-substituted alkanoate ethyl esters investigated when using (A) sulfuric acid as homogeneous catalyst and (B) sulfonic resin as heterogeneous catalyst. The insets in the figure are magnifications of the kinetics during the first 10 min (A) and 35 min (B).

3.2. Transesterification reaction rate and length of the alkyl acid chain

Fig. 4 compares the yields to the non-substituted methyl ester using sulfuric acid with those involving sulfonic resin, respectively. The insets in the figures represent a magnification of the kinetics during the first minutes of the reaction. The intrinsic reaction rate of the homogeneous sulfuric acid is much higher than the active sites of the resin [7,10,11,15] and in order to obtain comparable yields, the amount of homogeneous catalyst used was almost two orders of magnitude smaller than that used for the resin. In the case of the homogeneous reaction (Fig. 4A), the yield rapidly decreases as the number of carbon atoms increases up to when the acid chain of the ester is 5 carbon atoms long (ethyl hexanoate). Beyond this ester yield to methyl ester for C5, C6, and C8 esters are quite similar. The yield for the hexadecanoate is slightly smaller than that of pentadecanoate. By contrast, in the case of the heterogeneous catalyst (Fig. 4B) the behavior does not parallel that of sulfuric acid. Beyond the ethyl pentanoate yield to methyl ester decreases as the length of the chain become larger. For the larger ester investigated, ethyl hexadecanoate, the yield to methyl ester

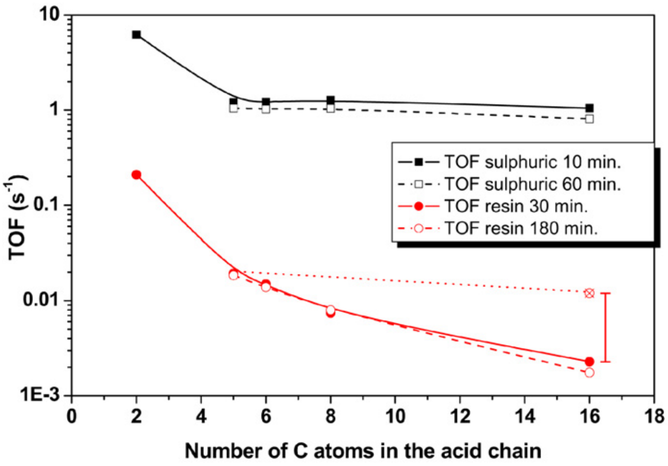


Fig. 5. TOF values obtained when sulfuric acid or acid resin are used as catalysts in the transesterification of non-substituted alkanoate ethyl esters: (■, □) for sulfuric acid and (●, ○) for acid resin. The TOF values were calculated for two different periods of time.

is much lower than that expected for a behavior parallel to that of homogeneous catalyst.

In the case of Fig. 5 the TOF numbers for the different esters were represented, both for the homogeneous and the heterogeneous cases. They were calculated by assuming that all the acid groups of the resin can participate in the reaction. For the homogeneous case they were calculated by using the yield at 10 min. of reaction and for the resin at 30 min. However for the sake of comparison the data at 60 min and 180 min, respectively, were also included. The latter were similar to that obtained at shorter reaction times what indicates that they were still valid as differential reaction rates (except for the case of the ethyl acetate case that showed very large yield, out of the differential regime). Fig. 5 shows that in the case of homogeneous reaction the trend follows the well reported behavior: a plateau is reached as the length of the chain is longer [7]. In the case of the solid resin, the leveling off observed in the homogeneous case for ester longer than 5 carbon atoms is no longer visible and the reaction rate keeps on decreasing as the chain become longer. The symbol ⊗ represents the hypothetical solid resin value for hexadecanoate case if the behavior was parallel to the homogeneous case.

When explaining the behavior shown in Fig. 5 by the sulfonic resin, one can, in principle, must consider the swelling of the resins and diffusional restrictions (inner or external). Swelling of the resins is a well-known event that may occur to a larger or smaller extent in polymeric resins when contacted with polar solvents: different interactions between the solvent and the groups of the polymer chain, especially sulfonic groups, result in the solvation of the polymer chains by the polar molecules. The hydrogen bond predominates, but other forces such as electron pair donation and non-specific forces may also be involved. Solvation may be accompanied by the penetration of the polar molecules into the pores defined by the intertwined polymeric chains that may stretch out the resin framework [16,17]. The different degree of swelling caused by the different molecules used in this study may determine the accessibility of the reactant molecule and therefore the reaction rate.

To test whether the swelling has an effect on the transesterification rate, two types of experiments were conducted. The swelling degree of the resin when immersed in methanol, in the esters with different polarity and in the methanol/ester solution with the same molar ratio used for the reaction was measured as the increase in the volume of the resin before and after immersion in the liquid. The change of volume was determined as follows: 2 g of the resin was placed in a sealed bottle and the height reached was measured. The solvent was then introduced into the flask until 2/3 of the flask volume was reached. After 24 h, the height of the swollen resin stabilizes and was measured. The increase was associated with the swelling degree. The degree was 17, 25, 11 and 12% for methanol, ethyl acetate, ethyl octanoate, and ethyl hexadecanoate respectively. The differences between the ethyl acetate and the ethyl hexadecanoate were even smaller if methanol was mixed with them (as occur in the reaction mixture). Then the swelling degree was 20 and 18%, that indicates that swelling is defined by the presence of methanol rather that due to the esters. Summarizing it can be concluded that the swelling degree is rather similar for all the molecules irrespective of the polarity of the solvent molecules and that the differences in accessibility of the different esters are therefore expected to be rather small. A second type of experiments also verified that the order of the addition (methanol first or ethyl hexadecanoate first) does not change the reaction rate. In short, the swelling of the resin can be discarded as the main cause of modification of the reaction rate.

It can also be argued that diffusional limitations can explain the decrease in the reaction rate in the heterogeneous reaction: more voluminous esters are more likely to be affected by external and inner mass transfer restrictions. These problems can be discarded because of the following. In order to assess on the external mass transfer restrictions, the rate obtained at shorter agitation speed (600 rpm) for the ethyl hexadecanoate (the larger ester) was determined and found to be 0.0021 s^{-1}, similar to the value represented in Fig. 5 (0.0019 s^{-1}) that was obtained at 1000 rpm. This data precludes the mass transfer distortion in the determination of the reaction rate of Fig. 5. Moreover the reaction rate for ethyl hexadecanoate was also determined by using larger resin particle size ($0.15 < \varnothing < 0.18$) than that used for Fig. 5 ($\varnothing < 0.106$). The TOF number was found to be 0.0021 s^{-1} that indicates that Fig. 5 result is not affected by inner mass transfer restrictions.

The absence of inner diffusional restrictions is not surprising if one take into account the mean pore size of the resin deduced from the N_2 isotherms which is around 40–50 nm. The immersion of the resin in the esters and/or in methanol scarcely modifies its textural properties since the swelling degree of the resin was small. The textural properties determined by N_2 isotherms must therefore be rather similar to that described by the N_2 isotherms. The largest dimension of the ethyl hexadecanoate, the longest ester, was estimated by the Gaussian program [20]. This dimension corresponds to the fully unfolded ester. Considering the length of the C–C, C=O and C–O bonds, the largest dimension is around 2.45 nm, more than one order of magnitude smaller than the mean pore size of the resin. It should be also taken into account that from the diffusion point of view this ester can be also considered a cylinder 2.54 nm long whose cylindrical base is defined by the ester group. Moreover the C16 ester can adopt folded configurations because the chain is flexible. Therefore, the ester can even diffuse through the pores in more favorable configurations. But even assuming that the ester occupies a volume defined by a sphere with a diameter of 2.45 nm, diffusion limitations within the catalyst pores can be considered negligible.

If diffusional restrictions cannot be the origin of the differences between sulfuric acid and resin catalyst, another explanation is required. Similar discrepancies between homogeneous and heterogeneous catalysts have been found by Goodwin and coworkers [7], albeit when studying the esterification of linear alkyl carboxylic acids with different chain length. Considering the close similarities in the reaction mechanism, the same arguments can, in principle, be applied to the transesterification reaction. The different behavior was explained by the "conformational levelling" effect that takes place in the homogeneous case, and it is absent in the heterogeneous reaction. The explanation, according to Goodwin and

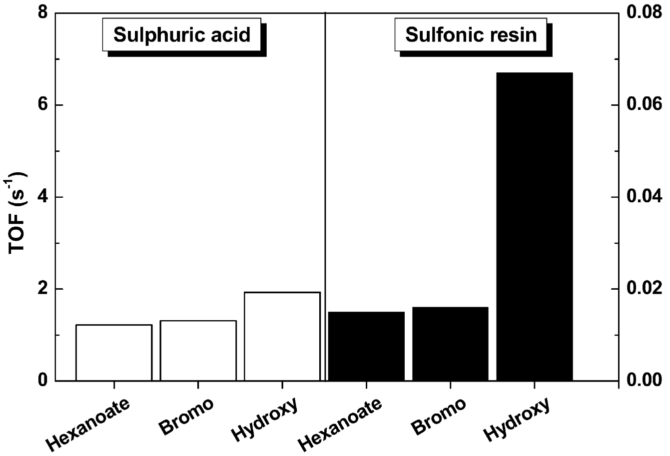
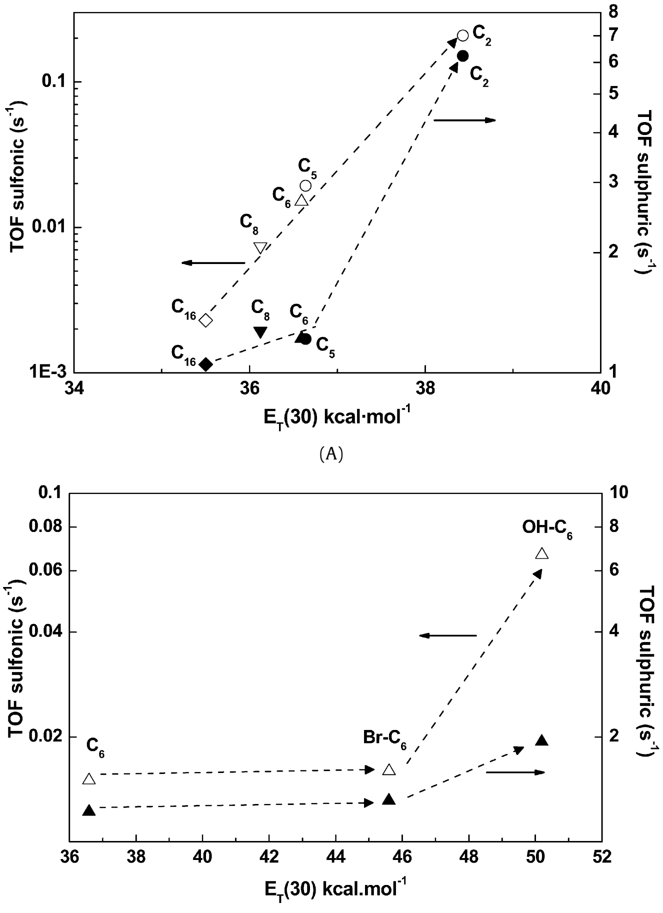


Fig. 6. TOF values obtained when sulfuric acid or acid resin are used as catalysts in the transesterification of hexanoate ethyl ester and bromo and hydroxy hexanoate ethyl esters.

coworkers is as follows [7]: a first aspect to consider is the rate determining step of the reaction. This is the nucleophilic attack of the alcohol on the carbon atom of the protonated carbonyl group (in the case of esterification, the carbonyl group belongs to a carboxylic group, and to an ester in transesterification). A requirement of this step is for methanol to approach the activated carbonyl group. The second aspect to consider is the steric hindrance that in principle is influenced by the size of the chain. Thus, a larger alkyl chain results in larger constraints of the alcohol molecule approaching the activated ester group. In the case of homogeneous reaction, the steric effect is also modulated by conformational effects [7,21,22] that minimize these constraints. Longer chains are flexible for adopting other preferential conformations. The conformational minimization is negligible when compared with steric hindrance for a chain with fewer than 5–6 carbon atoms, but when the length of the chain becomes longer it starts to be significant. In other words, the acid chain with more than 6–7 carbon atoms can adopt conformations that allow the methanol to reach the protonated carbonyl group as easily as with a shorter chain. As a result of this conformational flexibility, a leveling is reached in the reaction rate. This is possible in the case of homogeneous catalysis. However, it is absent in the case of heterogeneous catalyst because following Goodwin et al.'s suggestion for esterification reactions [7], the capacity to adopt another preferential conformation is restricted. The activated carbonyl group is now anchored onto the acid sites of the resin and surrounded by polymer chains. The freedom of the long acid chains of esters to adopt other conformations that facilitate the approach of methanol to the activated carbonyl is limited, and therefore steric hindrance remains a key factor in inhibiting the reaction. As a result, the heterogeneous reaction rate keeps on decreasing with the length of the acid chain, whereas it remains constant for the homogeneous case. The next section shows that this hypothesis must be reconsidered and/or completed by considering the possibility of hydrophobic repulsion between the activated ester chain and the sulfonic groups of the resin.

3.3. *Transesterification reaction rate and polar groups in the acid chain*

Fig. 6 shows the intrinsic reaction rate of ethyl bromohexanoate and ethyl hydroxyhexanoate when compared with that of ethyl hexanoate. White columns represent the values obtained when using sulfuric acid and darker columns when using the solid resin as catalysts. From the results in Fig. 6, it can be concluded that, in the case of homogeneous catalysis, an increase in the polarity of the ester molecule does not result in a noticeable increase in the reaction rate. In the case of the solid resin, the presence of the hydroxyl group results in a remarkable improvement of the reaction rate, whereas the Br group has only a small effect.



(A)

(B)

Fig. 7. (A) TOF values vs. $E_T(30)$ values of the different ethyl esters investigated: (■, □) acetate; (●, ○) pentanoate; (▲, △) hexanoate; (▼, ▽) octanoate; (◆, ◇) hexadecanoate. (B) TOF values vs. $E_T(30)$ values of the hexanoate, bromohexanoate and hydroxyhexanoate ethyl esters. White symbols indicate the reaction performed with sulfuric homogeneous catalyst and open symbols with heterogeneous sulfonic resin.

In the case of ethyl hydroxyhexanoate, it should be noted that other products besides methyl 6-hydroxyhexanoate were also formed. Those are the products derived from the transesterification of ethyl hydroxyhexanoate with itself and from the transesterification of methyl hydroxyhexanoate with itself and with ethyl hydroxyhexanoate. These reactions result in the formation of two hydroxydiesters with 13–14 C atoms that were detected by GC. If these products are considered, then the relative conversion of ethyl hydroxyhexanoate with respect to that of ethyl hexanoate was slightly higher with both homogeneous and heterogeneous catalyst. The contribution of these compounds was of the order of 5%, but in the heterogeneous case the differences are more intense. So the conclusions derived from Fig. 6 are still valid even if the formation of other products is taken into account.

Fig. 7 compares the reaction rate with the $E_T(30)$ values. It can be observed that in the case of linear non-substituted ethyl esters (Fig. 7A), conversion decreases upon the decrease of the polarity of the acid chain of the ester for both homogeneous and heterogeneous cases. But for the homogeneous the dependence is defined by the conformational leveling effect and not by the polarity of the ester: beyond the C_5 ester the trend reaches a plateau and rate of C_{16} ester is similar to that of C_5 although there is a difference of more than 1 kcal/mol in $E_T(30)$ value. In the case of the solid resin, there is a logarithmic dependence between the reaction rate and the polarity and the TOF number decreases upon the $E_T(30)$ value of the ester. We will return to this point later to discuss it deeper.

In the case of the bromohexanoate ester, the presence of a Br group at the end of the hexanoate chain results in an increase of ca. 9 $\text{kcal}\,\text{mol}^{-1}$ with respect to that of ethyl hexanoate (see Fig. 7B). This increase in polarity does not result in a remarkable increase in conversion either in the homogeneous reaction or in the heterogeneous reaction. By contrast, the presence of a hydroxy group increases ca. 14 $\text{kcal}\,\text{mol}^{-1}$ its $E_T(30)$ value (ca. 5 $\text{kcal}\,\text{mol}^{-1}$ more than the Br substituted ester) and this results in a ca. 7-fold increase in the reaction rate of methyl ester formation when using the sulfonic resin and a very small increase when using sulfuric acid (only ca. 2-fold).

Summarizing, in the case of acid solid resin there is a dependence of the intrinsic reaction rate with the polarity and with the presence of polar groups with HBD–HBA properties whereas there is not such correlation for the homogeneous acid catalyst.

4. Discussion

When looking for hypotheses that explain the effect of the polarity on the reaction rate we consider that the reaction mechanism must be taken into account. The reaction mechanism for the homogeneous catalysts is well known. However the heterogeneous case has been recently unveiled. It has been recently reported that the reaction mechanism of esterification and transesterification by heterogeneous catalyst follows the same steps as the homogeneous case [7,15,18,19,23]. In Scheme 1, this now widely accepted mechanism of transesterification of ethyl esters by methanol in the presence of a sulfonic resin is presented (the steps for the esterification reaction with methanol would be similar, but involving carboxylic acids). The principal peculiarities between heterogeneous and homogeneous mechanisms refer to the following two aspects: firstly, the activation of the carbonyl group of the ester comes with the chemisorption of the ester molecule on the Brønsted acid site. This chemisorption takes place by the acid attack on the O atom of carbonyl group forming the protonated carbocation intermediate. The second aspect refers to the Eley–Rideal model to account for the nucleophilic attack of the methanol molecule on the carbocation of the activated ester. As in the case of homogeneous system, this is the rate determining step [7,15,18,19,23]. Although methanol can also be chemisorbed on the Brønsted acid sites by the sulfonic attack on the O atom of the methanol molecule, the methanol involved in the rate determining step is not chemisorbed, but in the liquid medium present in the pores of the solid catalyst. These are the key peculiarities of the heterogeneous mechanism. The rest of the steps are similar to the homogeneous reaction, none of them are the rate determining step: inner rearrangement of protons and, finally, the deprotonation of the complex with the corresponding formation of the new ester and the recovery of the catalytic species.

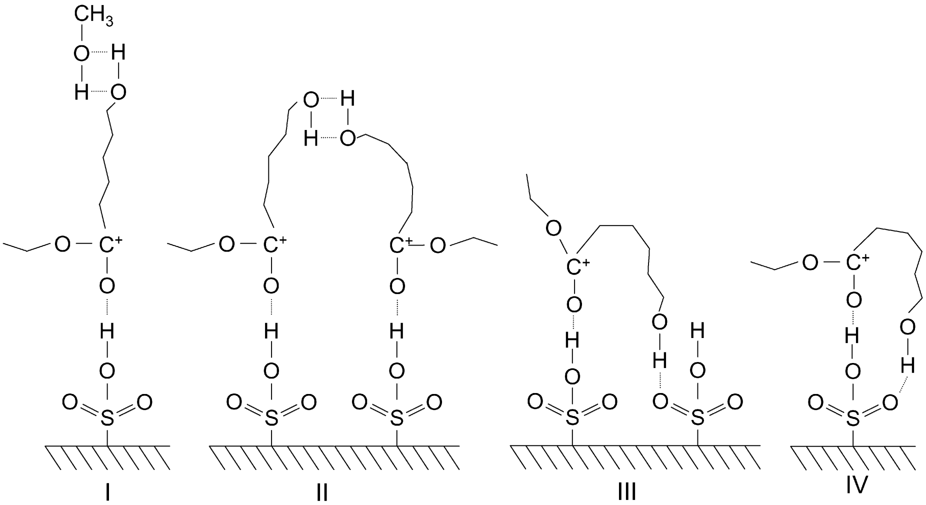
Considering this mechanism, we hypothesized that any variation in the polarity of the acid chain of the ester that helps to stabilize the chemisorbed activated intermediate participating in the rate determining step will favor the reaction: the rate determining step is faster as the concentration of the chemisorbed species is larger.

We propose that the dependence of the rate for solid resin with polarity described in Fig. 7A can be explained, besides by steric constraints, by repulsion effects. We propose that if long alkyl acid chains are involved, the stabilization of the activated complex is less favored because of the increase of the repulsion between the long chain of activated ester and the surrounding species (either at the surface of the resin or liquid within the pores). The repulsion is the result of the preferred chemisorption of methanol over the resin or the preferred presence of methanol in the pores. For the long ester molecule to be an activated complex it must displace the methanol out of the surface sites of the resin surface breaking the very strong HBD and HBA interactions established between the sulfonic groups and the methanol molecules and between the liquid methanol molecules themselves present within the pores. This repulsion depletes the surface concentration of the activated complex involved in the rate determining step for esters with larger acid chains with respect to those with shorter chains. This effect must also be taken into account, besides steric constraints, when explaining the lower reaction rate of long alkyl acid chain esters.

Another hypothesis that can be proposed is that the larger intrinsic reaction rates of acid homogeneous catalysts is related with the fact that the acid species are not concentrated on a polar surface but dispersed in the liquid and therefore the approach of the acid catalytic species to the ester group is not inhibited by any repulsion effect.

Fig. 7B showed that the presence of polar groups in ester chain with capacity of building up HBD and HBA interactions (like OH group) remarkably increases the reaction rate. On the contrary when the polar group does not show that capacity the reaction rate is scarcely affected. We propose that HBD and HBA interactions between the OH group of the ester chain and other groups present close to it stabilize the species involved in the rate determining step of the reaction. Scheme 2 describes some of the configurations of the chemisorbed activated complex derived from the ethyl 6-hydroxyhexanoate ester stabilized through HBD and HBA interactions with other species in its close vicinity. Others species can be proposed but for the sake of simplicity they are not included because the main guidelines of our interpretation are not altered. Species I describes the H-bonds that can be formed with the methanol molecules present in the liquid medium filling the pores of the solid. A similar picture can be drawn, albeit with the hydroxyl group of the other hydroxyl-ester molecule present in the liquid. Species II depicts the H-bonds that can be formed between the OH-ending of two supposedly adjacent activated ester molecules, although those species should be less likely. Species III and species IV describe the H-bonding of the OH-ending of the activated complex with the adjacent sulfonic group and with the self-activating sulfonic group. These species summarizes other configurations that can be proposed and that display HBA–HBD interactions with polar groups present at the surface of the resin or with chemisorbed alcohol (methanol or ethanol) molecules. Since the species I and II can be also present in the homogeneous catalysis, we propose that the interactions described by species III and IV, or others alike, are more responsible of the stabilization of the activated complex involved in the heterogeneous rate determining step. In other words it is the HBD–HBA interactions of the ester chain of activated complex with methanol in the pores and with sulfonic groups at the surface of the resin that notably improves the reaction rate. The increase is much more modest if the acid chain cannot establish these H-bonding interactions like for instance the Br-substituted ester. We cannot discard that the transition state of the rate determining step may also be affected by any of these interactions, but this hypothesis cannot be assessed with the experimental evidence provided in this work.

The information derived from this investigation can be extrapolated to other situation like of the effect of the polarity of the carboxylic acid chains on the esterification reaction and the effect of the polarity of the alcohol moiety of the ester on the transesterification reaction. The same type of attractive and repulsive forces and H-bonding interactions can be proposed in such cases. However, extrapolation to the polarity effect of the reacting



Scheme 2.

alcohol molecule in the transesterification and esterification reactions cannot be done. In principle, according to the Eley–Rideal mechanism, the chemisorption of the alcohol molecule is not required and the effects described here refer to the stabilization of a chemisorbed molecule. The authors are unaware of any research conducted comparing the effect of the length and of the polarity of the alcohol chain on the reaction rate in both homogeneous and heterogeneous reaction rates, and therefore cannot comment on this aspect.

5. Conclusions

The reaction rate of transesterification catalyzed by solid acids decreases upon increasing the length of the alkyl chain whereas for homogeneous acids reaches a plateau for esters with acid chains larger than 5 atoms. We propose that this trend in heterogeneous catalyst is explained not only because steric hindrances but also because of the repulsion between the non-polar chain of the ester with the polar acid groups on the catalyst surface and/or with the liquid methanol molecules present in the catalyst pores.

Repulsion or H-bonds effects are of no importance in the case of homogeneous acid catalyst because the active intermediate is not attached to a polar surface and this explains the larger intrinsic reaction rates of homogeneous acid catalysts when compared to those of solid acids.

The presence of functionalities in the ester chain with capacity to build up H-bonds, for instance hydroxy substituents, remarkably increases the transesterification reaction rate when a heterogeneous acid catalyst is used. We propose that the chemisorbed intermediate participating in the rate determining step of the reaction is stabilized by the formation of H-bonds with the acid groups present at the surface of the catalyst and/or with the liquid methanol molecules in the pores. This leads to a larger surface concentration of the active intermediate and therefore to an improvement of the reaction rate. The presence of other polar functionalities but without HBA–HBD properties does not have this positive effect.

Acknowledgments

Financial support from the Spanish Ministry of Science and Innovation through the projects BIOGLICAT (ENE-2006-15116-C04-01) and CTQ-2005-00114/BQU is grateful acknowledged. D.M.A. thanks the Comunidad de Madrid for a pre-doctoral fellowship. Ms. Laura Barrio Pliego is also thanked for her help in determining the size of the esters.

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