

Esterification of stearic acid by isomeric forms of butanol in a microwave oven under homogeneous and heterogeneous reaction conditions



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In this paper the influence of conventional and dielectric heating on the esterification of stearic acid by butanol has been studied. The influences of different isomeric forms of butanol, a catalyst and conditions of reaction (homogeneous *versus* heterogeneous) upon esterification have been investigated. The difference between conventionally or dielectrically heated reactions has been studied. For heterogeneous reactions a significant temperature enhancement effect is observed. This effect can be enlarged by the application of heat captors, which have been mixed or impregnated with catalyst. Further rate enhancements are realised by the use of a combination of microwave heating and ultrasound for heterogeneously catalysed reactions.

Introduction

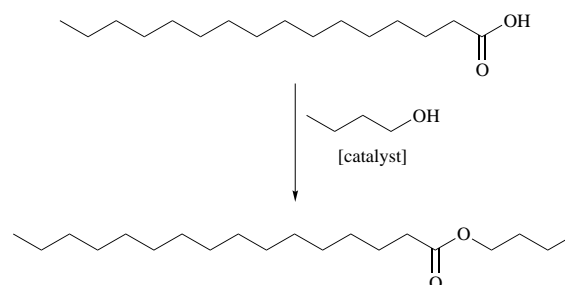
In the past ten years since the publication of Gedye *et al.*¹ there has been considerable interest in the application of microwave heating upon chemical reactions. After much debate² there seems to be general agreement that in most cases microwave heating can only give rise to different temperature regimes which can be used in a profitable way, for instance when reactions need to be rapid as in the case of the synthesis of radio-pharmaceuticals³ or when high temperatures need to be reached for the preparation of some inorganic compounds.⁴ In addition, microwave heating is ideal for solvent-free reaction systems: so called 'dry reactions'.⁵ Temperature effects are also the origin of the fact that a power input change can cause a difference in selectivity.^{2a,6} In this report, rates of esterification of stearic acid during microwave heating under homogeneous and heterogeneous conditions are determined. Specific focus is on whether claimed temperature enhancement effects can be used advantageously for improving yields of reactions or for the acceleration of reactions. Butyl esters of stearic acid are compounds which can be applied as a solvent, spreading or softening agent in polymers (plastics). In addition, they are used in the textile, cosmetic and rubber industries.⁷

Results and discussion

General strategy

The reaction studied is the esterification of stearic acid with butanol. In Scheme 1, the reaction is shown for *n*-butanol. The influence of various reaction conditions has been examined: the reactions can be carried out under homogeneous conditions with TPSA (toluene-*p*-sulfonic acid) as a catalyst, or a heterogeneous catalyst can be used. One objective is to investigate whether reactions under different conditions (homo- or heterogeneous media) would be influenced differently by the heating mode.

For reactions under homogeneous reaction conditions the effects of temperature variation and concentration of catalyst on reaction rates have been investigated. For reactions under heterogeneous conditions the effect of the nature of the catalyst and the effect of the simultaneous use of microwave and ultrasound irradiation have also been studied. The results of these studies are reported below.



Scheme 1 The esterification of stearic acid with *n*-butanol

Effect of catalyst

In the case of the uncatalysed reaction, a second-order dependence of the rate of esterification on the acid concentration was observed, due to autocatalysis of the esterification by the acid. When the concentration of alcohol is in tenfold excess of the concentration of acid, the rate for the uncatalysed reaction is given by eqn. (1). $k_{\text{obs,uncat}}$ can be measured and would be a

$$v = k_{\text{uncat}} [\text{alcohol}][\text{acid}]^2 = k_{\text{obs,uncat}}[\text{acid}]^2 \quad (1)$$

pseudo-second-order rate constant, because the acid is not only a reactant but is also an autocatalyst.

The rate of reaction, v , for the catalysed reaction is given by eqn. (2), in which k_{cat} is the rate constant of the catalysed

$$v = k_{\text{cat}} [\text{alcohol}][\text{acid}] = k_{\text{obs,cat}} [\text{acid}] \quad (2)$$

reaction and $k_{\text{obs,cat}}$ is the pseudo-first-order rate constant for the catalysed reaction.

Table 1 shows that the activation energy E_a for the esterification under homogeneous conditions is influenced by the presence of catalyst. The catalysed reaction has a lower activation energy than the uncatalysed reaction. However, there is no difference in activation energies with respect to the heating mode. The values of the activation energy are in accordance with literature values.⁸ The activation energies for both the esterification reactions (catalysed and uncatalysed) are the same irrespective of the heating mode when they are carried out under homogeneous reaction conditions. The fact that the heat-

Table 1 Activation energies for the catalysed and the uncatalysed esterification reaction between stearic acid and *n*-butanol^a

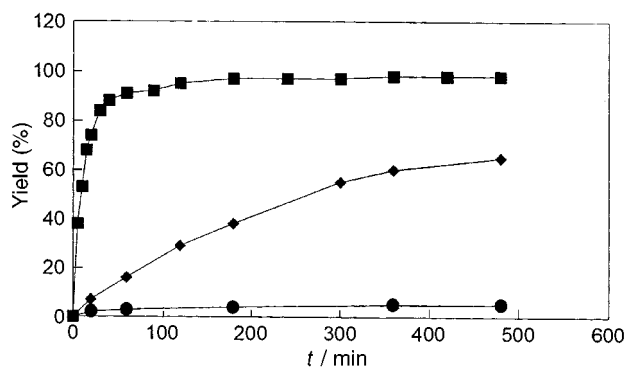
Reaction conditions	E_a (conventional)/ kJ mol ⁻¹	E_a (dielectric)/ kJ mol ⁻¹
No catalyst ^b	85	84
TPSA ^c	69	70

^a Error in the activation energies is approximately 3%, the rate constants from which the activation parameters were calculated are available as supplementary material from the British Library (SUP 57296, 2pp.). For details of the supplementary publications scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, Issue 1, 1997. ^b [Butanol] = 10 [acid]. ^c [Butanol] = 10 [acid] = 100 [TPSA].

Table 2 Influence of the heating mode on reaction yields for different esterification catalysts

Catalyst	Reaction time/min	$Y_{(d)}$ ^c	$Y_{(c)}$ ^d	$Y_{(d)}/Y_{(c)}$
TPSA ^a	60	91	89	1.0
Fe ₂ (SO ₄) ₃ ^b	120	71	50	1.4
TiBu ₄ ^b	120	78	60	1.3
KF ^b	120	85	64	1.3
Montmorillonite KSF ^b	120	95	82	1.2

^a Homogeneous reaction conditions. ^b Heterogeneous reaction conditions. ^c $Y_{(d)}$: yield (dielectrically heated). ^d $Y_{(c)}$: yield (classically heated).

**Fig. 1** Extent of esterification for the *n*-butyl (■), *sec*-butyl (◆) and *tert*-butylalcohol (●) as a function of reaction time; all reactions have been carried out at 140 °C

ing mode does not alter the rate of reaction has been observed previously.^{2c-e,9}

Effect of isomer

Under homogeneous reaction conditions the rate of reaction of the three butanol isomers has been followed, using either conventional or dielectric heating. The results of this study are depicted in Fig. 1. Under both conventional and microwave heating conditions the reactivity order is *n*-butyl > *sec*-butyl > *tert*-butyl alcohol. There is no increased reactivity of the isomeric forms of butanol under dielectric heating conditions, illustrating that the difference in reactivity towards esterification is, as in conventional heating, due to variation of the hydrocarbon moiety of the alcohols. The so-called antenna group effect^{2b} (specific activation of OH groups which could counteract the difference in reactivity) is therefore not apparent.

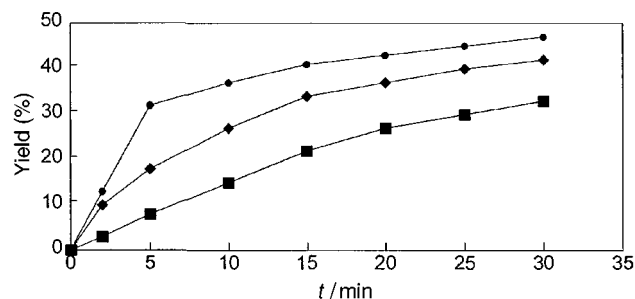
Reactions under homogeneous and heterogeneous conditions

Reactions under heterogeneous reaction conditions have been conducted at 140 °C only. It has already been established that reactions under microwave conditions are faster than those heated conventionally.¹⁰ The rate increases are most probably caused by a temperature enhancement effect. Reactions under

Table 3 Reactions with graphite (heat captor) and catalyst^a

Catalyst	t/min	Yield (%)
KF	5	82
Fe ₂ (SO ₄) ₃	5	75
TPSA	5	95

^a $T = 250\text{--}300$ °C, [butanol] = 10 [acid] = 100 [catalyst]. In each experiment 2 g of graphite was used.

**Fig. 2** Yields of esterifications with montmorillonite KSF catalyst at 140 °C for conventionally heated (■), microwave heated (◆) and microwave-ultrasound heated (●) reactions¹⁴

heterogeneous reaction conditions were carried out for 2 h at 140 °C. In Table 2 the results of this study are assembled.

It can be seen from Table 2 that the yields of the esterification reaction under homogeneous conditions are similar, irrespective of the heating mode. Under heterogeneous reaction conditions the dielectrically heated reaction shows a higher yield, after 2 h, than does the conventionally heated reaction mixture. The increase in yield after 2 h of heating can be expressed by a term $Y_{(d)}/Y_{(c)}$: the yield of the dielectrically heated reaction over the conventionally heated reaction. The effect is greatest for the catalyst iron(III) sulfate (1.4). For TiBu₄ and for KF a value of 1.3 was observed, and the smallest effect of dielectric heating was observed for montmorillonite ($Y_{(d)}/Y_{(c)} = 1.2$). Interestingly, the catalyst which gives rise to the lowest overall yield under conventional heating conditions seems to profit the most from dielectric heating. However, in all cases the heterogeneous catalysts do not surpass the homogeneous catalyst with respect to yield, except for montmorillonite KSF, but only after a prolonged reaction time. Differences due to dielectric heating only seem to be observed under heterogeneous reaction conditions.

Further use of temperature effects

Although the highest yields were observed for the homogeneously catalysed esterification reaction, the yields are greatly improved due to the heating mode when heterogeneous catalysts were used. The advantage of dielectric heating is caused by the fact that temperature enhancement effects can be realised.¹¹ In order to show the profitable use of microwave heating it would be required to demonstrate that temperature enhancement effects can be exploited. Therefore, a further study was carried out on catalysis in the presence of heat captors. Heat captors are materials which are known to be able to generate heat very efficiently and rapidly when heated by dielectric means. The use of these types of materials is interesting because very hot zones can be created at the surface of the solid particles without inducing a degradation of the products. The bulk temperature is kept constant if the concentration of the heat captor is low.

In Table 3 yields of the esterification reaction of stearic acid by *n*-butanol catalysed by TPSA, by iron(III) sulfate or by KF in the presence of graphite are shown. Rates of reaction increase dramatically when this heat captor is used in conjunction with microwave heating. Within 5 minutes, maximum yields of 75–95% of ester are observed. Again TPSA seems to be the most efficient catalyst. These high yields are caused by the fact that

Table 4 Catalysts used for the esterification reaction

Catalyst	Amount
TPSA	0.032 g (0.0002 mol)
Fe ₂ (SO ₄) ₃	0.16 g
TiBu ₄	0.14 g
KF	0.1 g
Montmorillonite KSF	0.8 g

the reaction mixture reaches very high temperatures during microwave dielectric heating. These temperatures have been measured during the experiment (see Fig. 3) and vary between 250–300 °C. Under conventional heating conditions these temperatures cannot be reached, even when heat captors are applied.

Simultaneous use of microwave heating and ultrasound

When reactions are carried out with the reaction mixture subjected to ultrasound, a mechanical effect is developed on the surface of the catalyst and this improves the mass transfer and hence higher yields of reactions can be observed.¹² If reaction mixtures were to be heated dielectrically while applying ultrasound, a further positive influence on the yields could be expected. This is a consequence of the concerted surface effects of both microwave heating (temperature effect at surface) as well as the mechanical effect of ultrasound on the surface of the catalyst. In Fig. 2 the extent of reaction as a function of time for the esterification of butanol with stearic acid with conventional heating, microwave heating and simultaneous microwave heating and sonication are shown, with montmorillonite as the catalyst. The rate of reaction shows the sequence MW-US > MW > conventional.

Conclusion

Rates of esterification are influenced by the presence of a catalyst. In the absence of a catalyst, the rate of esterification has a different dependence on the concentration of acid due to autocatalysis. The yields of esterification are different for the different butanol isomers, when the reaction mixtures are conventionally or dielectrically heated. The application of microwave heating does not alter the reaction rates for different isomers. Therefore there can be no specific activation under homogeneous reaction conditions, a finding noted earlier for esterifications.

Hence the explanation is that only heat effects can be exploited when dielectric heating is applied. This can be realised by carrying out reactions under heterogeneous reaction conditions. The yields of reaction using a heterogeneous catalyst such as Fe₂(SO₄)₃, TiBu₄, KF or montmorillonite KSF do not compare positively with the homogeneously catalysed reaction. However, yields are improved by application of dielectric heating compared with conventional heating. The optimal use of the different temperature regime can be further improved by the use of a heat captor and microwaves or heterogeneous catalysts and microwaves in conjunction with ultrasound.

In the first system a temperature effect (due to the heat captor) is induced. Concurrent application of ultrasound has a positive effect by causing increased mass transfer at the catalyst surface. Application of both techniques has a positive influence on the rate of esterification under heterogeneous reaction conditions.

Experimental

Equipment

All reactions which were dielectrically heated were subject to a frequency of 2.45 GHz in a Prolabo¹³ maxidigest 350 monomode cavity (power range 0–300 W) or in a microwave experimental design made in the ENSEIHT in Toulouse. The temperature was monitored by a gas thermometer which was

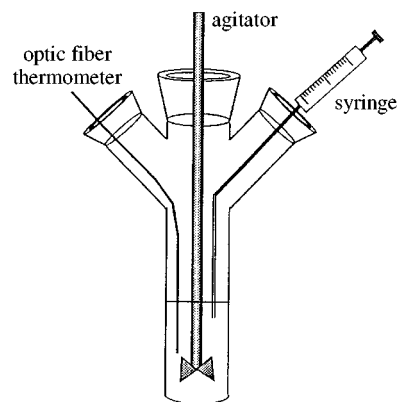


Fig. 3 Schematic representation of the experimental design of the reaction vessel used for this study

connected to a regulator. The regulator could control the temperature by choosing a high or low intensity of the microwave field (in commercial microwave ovens the temperature is controlled by an 'on-off' mechanism). In addition to a gas thermometer, the temperature was also monitored by a fibre optic thermometer. The experimental setup in the microwave oven is shown in Fig. 3. The degree of esterification was obtained by determination of the remaining fatty acid by a method described in 'AFNOR T 60–112'.[†] The AFNOR method has been validated by checking the amount of ester formed at the end of the reaction. When the reaction mixture was heated conventionally, this was carried out in a Pyrex reaction tube immersed in a thermostated oil bath, and fitted with a reflux condenser. The temperature was monitored with the aid of a thermocouple. The ultrasound–microwave system was described in detail by Chemat *et al.*¹²

Reagents

Stearic acid, butanol (normal, secondary and tertiary) and hexane were purchased from Merck and were all 99% + grade. TPSA (toluene-*p*-sulfonic acid) and graphite were purchased from Prolabo. Fe₂(SO₄)₃ and KF were obtained from Merck. In addition, montmorillonite KSF was obtained from Aldrich and tetrabutyl orthotitanate was purchased from Fluka. In all experiments the concentration of alcohol was chosen to be ten times that of the acid in order to maintain pseudo-first-order reaction conditions. A typical reaction mixture consisted of 0.02 mol of stearic acid (5.69 g) and 0.2 mol of butanol (14.8 g). All isomeric forms of butanol were used. Table 4 shows the catalysts and the typical amounts used in the reaction.

[†] AFNOR T 60–112 is an abbreviation of the standard method which has been used in the institute in Toulouse to determine the amount of free fatty acid.

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