Highly Selective Monomethyl Esterification of Terephthalic Acid by Use of Monocarboxylate Chemisorption on Alumina

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Summary When terephthalic acid, which had been chemisorbed on an alumina surface, was esterified in a stream of diazomethane, monomethyl terephthalate was obtained quantitatively.

RECENTLY, alumina and silica gel have been used as reaction media to control reactivity or selectivity. In one method the reagent is supported on an adsorbent to control its reactivity,[1] and in another the substrate is supported and treated with a reagent,[2] but applications of the latter method have been limited so far. We have already shown that substituents which were not directly bound to a solid surface adopted definite conformations on adsorption,[3] and so it should be advantageous to use adsorption to achieve regioselective reactions.

It is known, by i.r. and inelastic electron tunnelling spectroscopy,[4] that carboxylic acids chemisorb on alumina as symmetric, bidentate carboxylate ions and so the rest of the molecule will be remote from the alumina surface when the carboxylic acid chemisorbs. If only one carboxy-group of a dicarboxylic acid can be chemisorbed at a time then this will lead to two different reactivities of the carboxy-group. An attempt to cause only one of these carboxy-groups to react was made.

To a solution of terephthalic acid (**1**) in *NN*-dimethylformamide (DMF) was added alumina powder. The mixture was kept at 30 °C, with occasional shaking, for 8 h. Adsorption equilibrium, as measured by the u.v. absorption of the supernatant solution at 283 nm (ϵ 1840), was reached after 5 h. The alumina was filtered off and dried *in vacuo*. To a suspension of this alumina in 10 times its weight of n-hexane was introduced diazomethane in a stream of nitrogen.† After all the diazomethane had been consumed or had passed through the reaction vessel, the alumina was transferred to a column and washed with DMF. After concentration of the DMF eluate, the product was analysed by g.l.c.‡ No side reactions were observed.

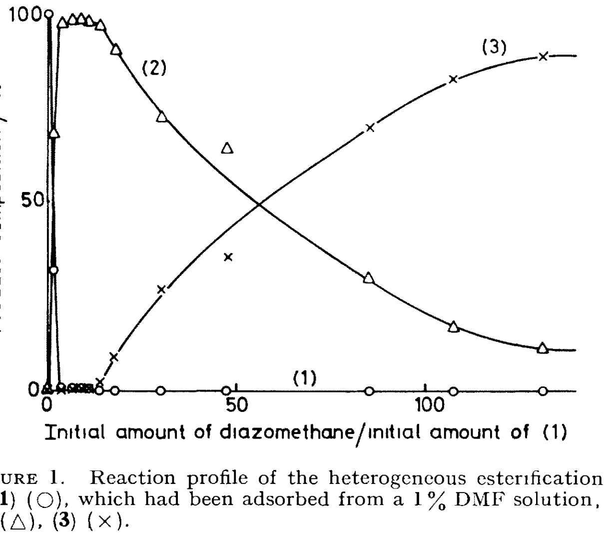

FIGURE 1. Reaction profile of the heterogeneous esterification of (**1**) (○), which had been adsorbed from a 1% DMF solution, (**2**) (△), (**3**) (×).

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† The solubilities of the substrate and the products are quite small in n-hexane. For example, no more than 0·15% of the reactants dissolved in n-hexane at the compositions indicated by the top of the curve for (**2**), when the adsorbed sample had been prepared from a 1% DMF solution of (**1**).

‡ The products were identified by comparison with authentic samples using a Chromosorb 101 column or a very short PEG 20M (*ca.* 10 cm) column at elevated temperatures.

TABLE Selective formation of monomethyl terephthalate (**2**)

Adsorbent	Concentration of (**1**) in DMF/%[a]	Amount of adsorbed (**1**)[b]	Selectivity for (**2**)/%[c]	Amount of diazomethane added[d]
Al_2O_3	0.100	10.0	99.0	121
	0.300	29.8	98.3	19.3
	1.00	77.6	97.6	8.43
	3.00	91.2	87.8	5.31
SiO_2	1.00	0.995	98.9	357
SiO_2–Al_2O_3[e]	1.00	24.1	96.6	29.3
SiO_2–Al_2O_3[f]	1.00	51.1	97.0	6.10
None[g]	1.00	—	50.2	1.43

[a] Solution : adsorbent = *ca.* 10 : 1 (w/w). [b] mg of (**1**) adsorbed per g of adsorbent, measured by the u.v. absorption of the supernatant solution at 283 nm. [c] The maximum value of $\{(\mathbf{2})/[(\mathbf{1})+(\mathbf{2})+(\mathbf{3})]\} \times 100$. [d] Mol diazomethane which give the maximum selectivity per mol of (**1**) adsorbed. [e] 13% Al_2O_3. [f] 28% Al_2O_3. [g] Homogeneous esterification in DMF solvent.

A plot of the composition of the product against the amount of diazomethane introduced is shown in Figure 1 which shows that diazomethane reacted exclusively with only one of the carboxy-groups of (**1**) in the first stage of the reaction. After the complete formation of monomethyl terephthalate (**2**), the second carboxy-group of (**2**) reacted very slowly to form dimethyl terephthalate (**3**).

The equal reactivities of the two carboxy-groups in unadsorbed (**1**) and (**2**) were confirmed as follows. The homogeneous esterification of (**1**) in DMF solution was carried out by introducing diazomethane and Figure 2 shows a plot of composition of the solution against the amount of diazomethane added. It shows a typical example of the two stage reaction proceeding *via* the intermediate (**2**), formed in about 50% yield at most.

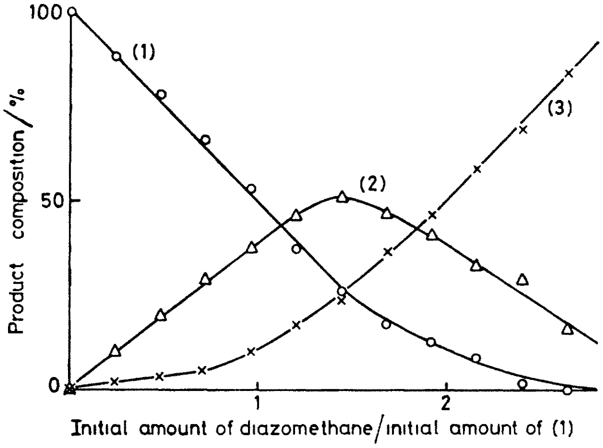

FIGURE 2 Reaction profile of the homogeneous esterification of (**1**) (○) in a 1% DMF solution, (**2**) (△), (**3**) (×).

It is reported that in a similar reaction[2] the selectivity of the reaction can be changed according to the amount of adsorption; therefore the effect of the amount of (**1**) adsorbed on alumina was examined. The results are shown in the Table together with the results obtained with adsorbents other than alumina. In all cases, the reactions took a similar course to that shown in Figure 1. The Table shows that when the amount of adsorption increased, the selectivity for formation of (**2**) decreased slightly. However the selectivities were much higher than in the homogeneous reaction.

Silica and silica–alumina were found to be as effective adsorbents as alumina for selective formation of (**2**) and the carboxylic acids seem to chemisorb in a similar manner to their adsorption on alumina.

This method is thus very effective for the monomethyl esterification of dicarboxylic acids which cannot adsorb both carboxylic acid groups at the same time.

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