

## On the acidity of liquid and solid acid catalysts. Part 3. Esterification of benzoic and mesitoic acids

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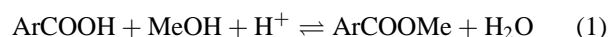
Methyl esters of benzoic and mesitoic acid have been prepared with high yields (>98 wt%) from the corresponding carboxylic acids + methanol in aprotic solvents over samples of H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> at 60 °C. The results show a high catalytic efficiency of the solids but also suggest an acid strength comparable to that observed in concentrated aqueous H<sub>2</sub>SO<sub>4</sub> (range >90 wt%) when the acid requirements for the esterification of analogous compounds in aqueous acid solutions are taken into account. Indeed, different reacting species, i.e., ArC(OH)<sub>2</sub><sup>+</sup> from benzoic acid and 2,4,6-triMe-ArC=O<sup>+</sup> from mesitoic acid are involved in the esterification, but the mesityl cation can be formed and esterified in the acidity ranges between 92 and 98 wt% H<sub>2</sub>SO<sub>4</sub>.

**Keywords:** esterification, benzoic acid, mesitoic acid, solid acid catalysts

### 1. Introduction

The reaction between an organic acid and an alcohol allows one to obtain by “esterification” a very large number of products of industrial interest and practical utility. It suggested extensive studies related to mechanism of reaction, substituent effects, dependence of rate on acidity, phenomena of equilibrium and reversibility [1–3].

In the recent years, solid acid materials and reaction conditions alternative to those conducted in aqueous solutions have been developed, accounting for practical, economical and environmental problems related to acid-catalysed reactions in strong acids [4–7]. In the present paper the esterification of benzoic acid with methanol (equilibrium (1)) over H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> has been tested because of the protonating ability [8–10] and catalytic properties [11,12] of these materials very similar to those observed in concentrated aqueous solutions of sulfuric acid [11,12]:



The esterification of mesitoic acid (or 2,4,6-trimethylbenzoic acid) with methanol was also attempted. The compound was chosen as an example of substituted benzoic acid, resistant to esterification under the usual aqueous experimental conditions, but easily converted in sulfuric acid >91 wt% [13]. The comparison with benzoic acid allows one to test the acid strength of the catalysts and their catalytic efficiency towards substrates with different acid requirements for the conversion reagents–products.

For an easier understanding of the results, the equilibria affecting the reacting species in concentrated aqueous acid solutions, are at first briefly discussed. The procedure

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adopted for determining parameters with a thermodynamic significance and the reasons for this choice are also given.

### 2. Ionizations of the reacting species in aqueous acid solutions

#### 2.1. Ionization of benzoic acid

The ionization of benzoic acid as a base (B) (equilibrium (2)) can be measured in concentrated aqueous solutions of sulfuric acid (range 70–100 wt%) where the solute exhibit basic properties compared with the solvent [14].



In the study of a weak base (B) undergoing protonation in non-ideal acid solutions (equilibrium (3)) the determination of  $pK_{\text{BH}^+}$  values with a thermodynamic significance is of interest [3,15,16]. From a practical point of view it requires the evaluation of the  $\log[\text{BH}^+]/[\text{B}]$  values and the additional knowledge of  $\log[\text{H}^+]$  and  $\log(f_{\text{B}}f_{\text{H}^+}/f_{\text{BH}^+})$  terms which appear in the thermodynamic equation (4) [16].



$$pK_{\text{BH}^+} = \log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+] - \log(f_{\text{B}}f_{\text{H}^+}/f_{\text{BH}^+}) \quad (4)$$

In this paper the parameters related to equilibrium of benzoic acid as B have been determined by

$$pK_{\text{BH}^+} = \log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+] + n_{\text{bb}^*} \text{Mc}(\text{B}^*), \quad (5)$$

where (i)  $\log[\text{BH}^+]/[\text{B}]$  are the available experimental data, (ii)  $\log[\text{H}^+]$  values are obtained from the degrees of dissociation of the acid in water ( $\alpha$  values), (iii)  $\text{Mc}(\text{B}^*)$ , defined by equation (6), is an “activity coefficient function”

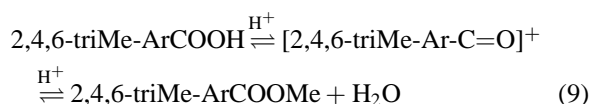
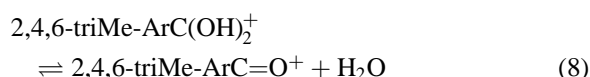
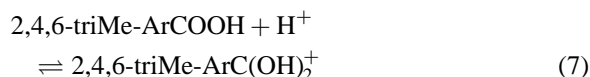
obtained by comparing a set of increasingly weaker bases with analogous or different structure protonating in a series of acid solutions [16]. Therefore, the  $\text{Mc}(\text{B}^*)$  function is a measure of the deviations from the ideality of the acidic medium under investigation, with reference to that of a weak base ( $\text{B}^*$ ) protonated at low acid concentrations and chosen as standard state.

$$\text{Mc}(\text{B}^*) = -\log(f_{\text{B}^*} f_{\text{H}^+} / f_{\text{B}^*\text{H}^+}). \quad (6)$$

It follows that the equilibrium of a weak base by equation (5) is described by two independent parameters ( $n_{\text{bb}^*}$ ) and ( $\text{p}K_{\text{BH}^+}$ ), whose values can be determined by the slope ( $n_{\text{bb}^*}$ ) and intercept ( $\text{p}K_{\text{BH}^+}$ ) of the plot ( $\log[\text{BH}^+]/[\text{B}] - \log[\text{H}^+]$ ) vs. the  $\text{Mc}(\text{B}^*)$  function. According to the Mc procedure,  $n_{\text{bb}^*} = 0.80$  and  $\text{p}K_{\text{BH}^+} = -6.3$  were estimated for the equilibrium (2) and obtained as average of the values observed on the analysis of the experimental data at different wavelengths [14].

## 2.2. Ionization of mesitoic acid

Mesitoic acid is resistant to esterification under the aqueous acid conditions used for the benzoic acid, but it can be easily converted in sulfuric acid >91 wt% [13]. This behaviour is consistent with a complex ionization which involves two processes [17]: the protonation (equilibrium (7)) and the conversion to the oxocarbenium ion (equilibrium (8)), the latter able to be esterified or hydrolysed (equilibrium (9)) [13]:



The ionizations (7) and (8) are in agreement with the observed freezing-point depression (van't Hoff  $i$  factor = 4) being twice as large as benzoic acid itself [18]. Also with the results obtained by UV [17], IR [19] and NMR studies [20] which support analogous ionizations. It is expected that sterically hindered acids can be easily esterified by the oxocarbenium ion for the linear  $[-\text{C}=\text{O}]^+$  group as site of the methanol attack [2,21]. However, strong acidic media are needed for equilibrium (8). In the equilibria of formic acid, for instance, the energetic values estimated for the protonation at the carbonyl oxygen atom and for the protonation at the hydroxy oxygen atom differ by ca. 28 kcal mol<sup>-1</sup> [22]. The  $\text{p}K_{\text{BH}^+}$  of equilibrium (8) defined by the thermodynamic equation (10) has been calculated by equation (11), using the experimental data of the species  $\text{MsC}(\text{OH})_2^+$  as (B) and  $\text{MsCO}^+$  as ( $\text{BH}^+$ ), observed between 90 and 100 wt%  $\text{H}_2\text{SO}_4$  [17]. The parameters obtained by the plot  $\log\{[\text{MsCO}^+][\text{H}_2\text{O}]/[\text{MsC}(\text{OH})_2^+][\text{H}^+]\}$

vs.  $\text{Mc}(\text{B}^*)$  are:  $\text{p}K_{\text{MsCO}^+} = -8.5$ ,  $n_{\text{MsCO}^+} = 0.95$  (Ms = mesityl group).

$$\text{p}K_{\text{MsCO}^+} = \log\{[\text{MsCO}^+][\text{H}_2\text{O}]/[\text{MsC}(\text{OH})_2^+][\text{H}^+]\} - \log(f_{\text{MsC}(\text{OH})_2^+} f_{\text{H}^+} / f_{\text{MsCO}^+} f_{\text{H}_2\text{O}}), \quad (10)$$

$$\text{p}K_{\text{MsCO}^+} = \log\{[\text{MsCO}^+][\text{H}_2\text{O}]/[\text{MsC}(\text{OH})_2^+][\text{H}^+]\} + n_{\text{MsCO}^+} \text{Mc}(\text{B}^*). \quad (11)$$

## 2.3. Ionization of alcohols

The equilibria of alcohols in aqueous acid solutions (equilibrium (3)) have been investigated by different techniques on the attempt to decrease the uncertainties affecting the degree of protonation [3,15,23–25]. The NMR data of ethanol available in the range 8–100 wt%  $\text{H}_2\text{SO}_4$  [24] and analysed by equation (5) allow one to deduce a  $\text{p}K_{\text{BH}^+}$  value of  $-2.10$  and  $n_{\text{bb}^*}$  of  $0.22$ . For ethanol and methanol, the latter one used as reagent in our esterifications, very similar basicity is to be expected. It is suggested from the results obtained from the previous studies where methanol and ethanol are compared [25].

## 2.4. The characterization of acidity by thermodynamic parameters

The equilibria of reacting species reported above have been analysed by a procedure which allows to obtain a reliable description of the acidic properties of the solvent. Also, satisfactory correlations between the protonation process of solutes and the dissociation of the solvent [16,26]. The key parameters of this procedure have been obtained by studying, separately, a number of HA (for  $\text{HA} = \text{CF}_3\text{SO}_3\text{H}$ ,  $\text{CH}_3\text{SO}_3\text{H}$ ,  $\text{HBr}$ ,  $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ) in ( $\text{HA} + \text{H}_2\text{O}$ ) mixtures as well as a number of B (for B = nitroanilines, carbinols, nitrobenzenes, sulfoxides, sulfonic acids, etc.) in ( $\text{B} + \text{HA} + \text{H}_2\text{O}$ ) mixtures. Then, by comparing the phenomena governing the equilibria of solutes and solvents. The main parameters obtained are as follows:

- (i) An *activity coefficient function of the solvent* (or  $\text{Mc}(\text{s})$  function) which has been determined by taking into account the dissociation of HA (equilibrium (12)) and the departure from ideality in the activity coefficient term of thermodynamic equation (13). For acid systems with known  $\text{p}K_{\text{HA}}$  and  $\alpha$  values, an  $\text{Mc}(\text{s})$  function by equation (14) has been derived:



$$\text{p}K_{\text{HA}} = \log[\text{HA}]/[\text{A}^-] - \log[\text{H}^+] - \log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}), \quad (13)$$

$$\text{p}K_{\text{HA}} - [\log[\text{HA}]/[\text{A}^-] - \log[\text{H}^+]] = n_s \text{Mc}(\text{s}), \quad (14)$$

where

$$\{\log[\text{HA}]/[\text{A}^-] - \log[\text{H}^+]\} = \{\log[(1 - \alpha)/\alpha^2 c]\},$$

$$\text{Mc}(\text{s}) = -\log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}) \text{ and } n_s = 1.$$

(ii) An *activity coefficient function of solutes* (or  $\text{Mc}(\text{B}^*)$  function) which has been determined by taking into account the protonation of B (equilibrium (3)) and the departure from ideality in the activity coefficient term of thermodynamic equation (4). In this case any two overlapping ( $\text{B}_1, \text{B}_2$ ) bases have been compared by equations (15) or by (15') and the  $n_{\text{b}_1, \text{b}_2}$  values relating all the indicators have been referred to that of a standard weak base ( $\text{B}^*$ ) [16,26]:

$$\begin{aligned} & \log[\text{B}_1\text{H}^+]/[\text{B}_1] - \log[\text{H}^+] \\ &= n_{\text{b}_1, \text{b}_2} (\log[\text{B}_2\text{H}^+]/[\text{B}_2] - \log[\text{H}^+]) \\ &+ \text{constant}, \end{aligned} \quad (15)$$

$$\log(f_{\text{B}_1} f_{\text{H}^+} / f_{\text{B}_1\text{H}^+}) = n_{\text{b}_1, \text{b}_2} \log(f_{\text{B}_2} f_{\text{H}^+} / f_{\text{B}_2\text{H}^+}). \quad (15')$$

(iii) The *acidic property of a solvent* obtained by the slopes of the plots of the  $\text{Mc}(\text{B}^*)$  (or  $\text{Mc}(\text{i})$ ) vs. the  $\text{Mc}(\text{s})$ . Indeed, these functions were found to be linearly related between them by equation (16) (or by equation (16')), with slopes values ( $n_{\text{is}}$ ) very different from unity:

$$\text{Mc}(\text{i}) = n_{\text{is}} \text{Mc}(\text{s}), \quad (16)$$

$$-\log(f_{\text{B}^*} f_{\text{H}^+} / f_{\text{B}^*\text{H}^+}) = -n_{\text{is}} \log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}). \quad (16')$$

Therefore, the  $n_{\text{is}}$  can be interpreted as a measure of the specific interactions between solutes and solvents in the proton transfer process from  $\text{H}^+\text{A}^-$  to  $\text{BH}^+\text{A}^-$ , or as a measure of the *protonating ability of an acidic medium*. The  $n_{\text{bb}^*}$  determined by equation (5) can equally be taken as parameters related to the acid–base interactions. In this case the process from  $\text{H}^+\text{A}^-$  to  $\text{B}^*\text{H}^+\text{A}^-$  (i.e.,  $n_{\text{is}} = 1 = n_{\text{bb}^*}$ ) is taken as unity and the  $n_{\text{bb}^*}$  values are referred to the  $\text{B}^*\text{H}^+\text{A}^-$  standard state.

The interactions between solid acids and probe molecules in the process ( $\text{solid-H}^+ + \text{B} \rightarrow \text{BH}^+$ ) have been exploited by analogous treatments of the equilibrium data [8–10]. For instance, the results obtained by nitroanilines adsorbed over samples of  $\text{HA}/\text{SiO}_2$  show that the  $n$  values, compared to those observed for analogous bases in aqueous acid solutions, differ by a factor of ca.  $10^4$ – $10^5$ . The  $pK_{\text{BH}^+}$  of indicators in both systems, instead, were found to be the same. The process ( $\text{pyridine} + \text{BH}^+ \rightarrow \text{B} + \text{pyridine-H}^+$ ), using pyridine as a back-titrating agent exhibit, in this case, the expected  $pK_{\text{BH}^+}$  values of the bases (i.e., pyridine and indicators) but a lower protonating factor [9]. It has been suggested that new equilibria related to the species (i.e.,  $\text{solid-H}^+$ ,  $\text{pyridine-H}^+$ ,  $\text{BH}^+$ ) are involved in the protonating process with pyridine, suitable to modify the acid–base interactions occurring in the previous one where analogous indicators and solid acids, without pyridine, are analysed.

According to the new experimental observations it seems reasonable to suggest that the *Hammett acidity functions*

defined by equation (17) [15] cannot be accepted as parameters related to “acidity” of concentrated aqueous acid solutions. It is essentially due to an incorrect evaluation of the parameters which characterize an “acidity function”:

$$\begin{aligned} H_x &= pK_{\text{BH}^+} - \log[\text{BH}^+]/[\text{B}] \\ &= -\log[\text{H}^+] - \log(f_{\text{B}} f_{\text{H}^+} / f_{\text{BH}^+}). \end{aligned} \quad (17)$$

Accounting for the equilibria of solvents, for instance, an  $\text{Ac}(\text{s})$  function (see equation (18)) which is *the extension of the pH scale* in concentrated aqueous acid solutions, can be derived. Accounting for the equilibria of solutes, an  $\text{Ac}(\text{i})$  (see equation (19)) but not an  $H_x$  function can be derived. It follows that  $\text{Ac}(\text{i})$  and  $H_x$  acidity functions differ by the  $n_{\text{is}}$  values, or by the parameters expressing the interactions between solutes and solvents.

$$\begin{aligned} \text{Ac}(\text{s}) &= \{-\log[\text{H}^+] + \text{Mc}(\text{s})\} \\ &= \{-\log[\text{H}^+] + \log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}})\}, \end{aligned} \quad (18)$$

$$\begin{aligned} \text{Ac}(\text{i}) &= \{-n_{\text{is}} \log[\text{H}^+] + \text{Mc}(\text{i})\} \\ &= \{-n_{\text{is}} \log[\text{H}^+] + \log(f_{\text{B}^*} f_{\text{H}^+} / f_{\text{B}^*\text{H}^+})\}. \end{aligned} \quad (19)$$

### 3. Experimental

#### 3.1. Materials

Purified samples of GRACE GmbH Silica Gel (90  $\mu\text{m}$  average particle size, 364  $\text{m}^2 \text{g}^{-1}$  ( $S_{\text{BET}}$ ), 1.14  $\text{ml g}^{-1}$  pore volume) have been obtained by washing the commercial material with aqueous solutions of perchloric acid, then with distilled water. Solvents, reagents and products have also been used after purification. Aqueous sulfuric acid solutions of various strengths were prepared by diluting the concentrated acid (Analar grade) and their percentage composition was determined by automatic potentiometric titrations against standard solutions of NaOH.

#### 3.2. Preparation and characterization of solid acid catalysts

(i) A known amount of silica gel powder was mixed with a known amount of aqueous sulfuric acid of appropriate concentration. After stirring for ca. 1 h the supernatant solution was removed by filtration and the wet catalyst was dried for two days between 105 and 180  $^\circ\text{C}$  in a stream of  $\text{N}_2$ , then stored in a dry apparatus. The acid percentage composition in the solids after impregnation was determined by automatic potentiometric titrations against standard solutions of NaOH and checked before use.

(ii) The BET surface areas (SA) of the loaded samples have shown a continuous decrease as the amount of sulfuric acid adsorbed by the solids increases. The observed values, using a starting silica gel powder with 364  $\text{m}^2 \text{g}^{-1}$  are 291, 214, 182, 136, 108 and 80  $\text{m}^2 \text{g}^{-1}$  for samples with acid loadings, respectively, of 1.37, 2.75, 3.30, 4.12, 4.52 and 5.07  $\text{mmol H}_2\text{SO}_4 \text{g}_{\text{catalyst}}^{-1}$ .

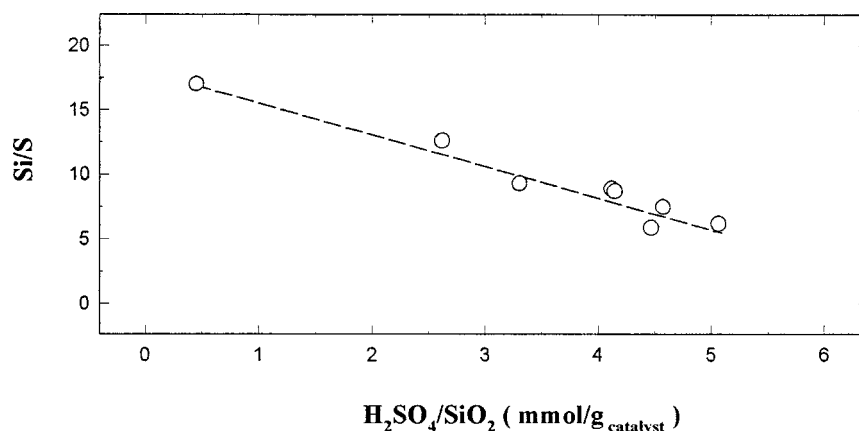


Figure 1. XPS data of the catalysts determined by XPS peak areas of Si 2p and S 2p: Si/S ratio vs. mmol  $\text{H}_2\text{SO}_4 \text{ g}_{\text{catalyst}}^{-1}$ .

(iii) The surface layers of the catalysts have been characterized by XPS measurements. On the analysis by pyridine chemisorption and investigation of the N 1s XPS band [27] the samples exhibit a single peak at 401 eV due to the strong Brønsted acid sites. On the analysis by the XPS peak areas of Si 2p and S 2p, the Si/S ratios were found to be proportional to the amount of sulfuric acid added to silica gel (see figure 1). Additional studies by UV, used for testing the protonation process of progressively weaker bases (B) have shown that chloro-nitroanilines and 3-substituted trinitroanilines can be converted in their conjugated acid ( $\text{BH}^+$ ) by samples with increasing acid loadings [8–10].

(iv) Measurements related to the adsorption equilibria have been performed by contacting at 60 °C a given amount of the catalyst with either a single chemical species or binary mixtures in toluene. The results for single chemical species have shown that methanol has the higher affinity for the catalyst and the order methanol  $\gg$  benzoic acid  $\geq$  methyl benzoate has been observed. For the adsorption of methyl benzoate and benzoic acid further results have been obtained by using the plots (mmol aromatic  $\text{g}_{\text{catalyst}}^{-1}$ ) vs. (molarity of aromatic). Linear trends with slope values of 2 and 8, respectively, are observed at low concentrations of aromatic (ca.  $<0.3 \text{ mol dm}^{-3}$ ), but a saturation limit between 0.3 and  $0.7 \text{ mol dm}^{-3}$ . In an analogous plot, the adsorption of binary mixtures methanol–methyl benzoate at low and high concentrations show a linear relationship with a slope value of 0.32. No saturation limit has been observed in this case. A peculiar and interesting feature related to adsorption equilibria, is that the catalysts exhibit an high adsorption power for water. Methyl benzoate is desorbed from the catalyst without hydrolysis when equimolar amounts of water are added to methyl benzoate–toluene mixtures.

### 3.3. Esterification of benzoic acid with methanol

Separate solutions of benzoic acid and methanol in toluene of appropriate concentrations were prepared using weighed amounts of solvent and reagents. The kinetic runs were performed in a well stirred thermostated reactor con-

taining weighed samples of the solvent, reagents and catalyst. Small amounts of the solution were drawn at different times and the samples, after dilution, were analysed by HPLC, using a Perkin–Elmer apparatus and a Lichrospher 100 (RP-18, 5  $\mu\text{m}$ ) column. The mixtures at the end of the reaction were also detected by GC and GC-MS, using an HP5 capillary column (300  $\mu\text{m}$  i.d., 30 m long, 95% methyl, 5% phenyl siliconic phase).

In table 1 the experimental details and the kinetic results are reported. Methyl benzoate as unique product of the reaction has been observed in all cases and in figure 2(a) a typical kinetic run is shown. The initial reaction rates ( $r_0$  values) have been estimated from the yields of methyl benzoate using different kinetic models in order to obtain a reliable form of the rate expression governing the reaction. All data suggest a first-order reaction with respect to the benzoic acid, in agreement with the adsorption equilibria of the reagents reported above. An inspection of the Carberry and Weeler–Weisz number [28] allows one to state that both liquid/solid and internal pore diffusion do not affect the overall reaction kinetics.

### 3.4. Esterification of substituted benzoic acids with methanol

The esterification of substituted benzoic acids over  $\text{H}_2\text{SO}_4/\text{SiO}_2$  has been performed by following experimental procedures and analytical methods analogous to those applied for benzoic acid:

- (i) Methyl mesitoate was obtained with high yields (98–99%) in short times from mesitoic acid and methanol, in toluene, over catalysts with different acid loadings. Mesitylene as by-product ( $<1\%$ ) has also been observed, due to acid-catalysed decarboxylation of mesitoic acid [17]. Indeed, according to results observed in concentrated aqueous sulfuric acid [17], mesitylene is the only product of the reaction when mesitoic acid in toluene, without methanol, is added to the samples of the acid catalysts. Unfortunately, the esterification of mesitoic acid at 70 °C shows a complicated kinetic behaviour at very short reaction times (figure 2(b)),

Table 1  
Esterification of benzoic acid with methanol over H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> in toluene.

Catalyst				Reaction		Results <sup>g</sup>		
Acid <sup>a</sup>	Acid <sup>b</sup>	T <sup>c</sup> (°C)	d (g)	Ratio <sup>e</sup>	T <sup>f</sup> (°C)	log r <sub>0</sub>	log k <sub>a</sub>	log k <sub>b</sub>
<i>(a) Acid loading</i>								
1.63	0.21	105	4	1:5	60	-3.95	-2.92	-2.78
2.16	0.28	105	4	1:5	60	-3.91	-2.99	-2.82
3.03	0.39	105	4	1:5	60	-3.81	-3.04	-2.75
3.32	0.43	105	4	1:5	60	-3.80	-3.07	-2.76
4.75	0.62	105	4	1:5	60	-3.93	-3.36	-2.79
1.51	0.19	180	4	1:5	60	-3.93	-2.85	-2.74
1.93	0.25	180	4	1:5	60	-3.82	-2.85	-2.70
2.71	0.35	180	4	1:5	60	-3.73	-2.91	-2.67
3.30	0.43	180	4	1:5	60	-3.69	-2.96	-2.65
5.25	0.68	180	4	1:5	60	-3.90	-3.38	-2.66
<i>(b) Temperature of reaction</i>								
3.03	0.39	105	4	1:5	50	-4.07	-3.31	-3.01
3.03	0.39	105	4	1:5	60	-3.81	-3.05	-2.75
3.03	0.39	105	4	1:5	70	-3.53	-2.76	-2.46
4.75	0.62	105	4	1:5	50	-4.24	-3.67	-3.10
4.75	0.62	105	4	1:5	60	-3.93	-3.36	-2.79
4.75	0.61	105	4	1:5	70	-3.73	-3.16	-3.59
<i>(c) Amount of catalyst</i>								
4.75	0.31	105	2	1:5	60	-4.21	-3.35	-2.78
4.75	0.47	105	3	1:5	60	-4.08	-3.39	-2.82
4.75	0.62	105	4	1:5	60	-3.93	-3.36	-2.79
<i>(d) Ratio ArCOOH: MeOH</i>								
4.75	0.62	105	4	1:5	50	-4.24	-3.67	-3.10
4.75	0.64	105	4	1:10	50	-4.15	-3.59	-3.02
4.75	0.62	105	4	1:5	60	-3.93	-3.36	-2.79
4.75	0.61	105	4	1:11	60	-3.91	-3.33	-2.76

<sup>a</sup> Acid = mmol H<sub>2</sub>SO<sub>4</sub> g<sub>catalyst</sub><sup>-1</sup>.

<sup>b</sup> Acid = mol dm<sup>-3</sup> of H<sub>2</sub>SO<sub>4</sub>.

<sup>c</sup> Temperature of dehydration of the catalysts.

<sup>d</sup> Amount of catalyst (g) used in the reaction.

<sup>e</sup> Ratio benzoic acid: methanol; [ArCOOH] = ca. 0.5 mol dm<sup>-3</sup>.

<sup>f</sup> Temperature of esterification.

<sup>g</sup> r<sub>0</sub> values = initial reaction rates (mol dm<sup>-3</sup> s<sup>-1</sup>) estimated from the yields of methyl benzoate; log k<sub>a</sub> = log(r<sub>0</sub>/[acid]), (s<sup>-1</sup>); log k<sub>b</sub> = log(r<sub>0</sub>/[acid] × f) (f = SA<sub>cat</sub>/SA<sub>SiO<sub>2</sub></sub>), (s<sup>-1</sup>). The esterification of ArCOOH + MeOH over H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> (6 g dried at 105 °C) in methanol at 25 °C shows at a given acid concentration the following log r<sub>0</sub>, log k<sub>a</sub>, log k<sub>b</sub> values: at 2.07 (0.423 mol dm<sup>-3</sup>) -4.57, -3.84 and -3.67; at 3.10 (0.642 mol dm<sup>-3</sup>) -4.44, -3.88 and -3.60; at 4.23 (0.860 mol dm<sup>-3</sup>) -4.43, -4.00 and -3.54. A value log k<sub>obs</sub> = -2.95 has been found in the esterification of ArCOOH in methanol added with H<sub>2</sub>SO<sub>4</sub> (0.348 mol dm<sup>-3</sup>).

also observed at lower reaction temperatures or with different samples of acid-loaded catalysts.

- (ii) Tests related to synthesis of diesters from phthalic acid and phthalic anhydride with methanol have shown that quantitative yields of products can be obtained in few hours when the diesterification was performed in refluxing benzene over H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> using acid loadings >4.5 mmol H<sub>2</sub>SO<sub>4</sub> g<sub>catalyst</sub><sup>-1</sup>. The low solubility of the phthalic acid in benzene does not affect the conversion reagent-products.
- (iii) A comparison between Amberlyst-15 and H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> as catalytic systems was also attempted, using samples with analogous acid sites concentration (4.9 mmol H<sup>+</sup> g<sub>catalyst</sub><sup>-1</sup>). The results over Amberlyst-15 at 70 °C show that methyl mesitoate with high yields (99%) was obtained when mesitoic acid: mmol H<sup>+</sup> ratios be-

tween 1:12 and 1:15 were used. The 1:2 catalytic ratio suitable for high conversion reagent-products over H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub>, exhibits by Amberlyst-15 yields of product ca. <3%.

#### 4. Results and discussion

The esterification of saturated and unsaturated acids with alcohols over Nafion [4,29], Amberlyst [30,31], zeolites [32-34], heteropoly acids [35,36] has already been reported together with the advantages or disadvantages of a catalyst when selectivity, conversion, by-products, recycle of the catalysts, etc. are taken into account. A recent attempt sought to exploit the acidity of solids by studying samples of H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> has been developed [8-12] and the

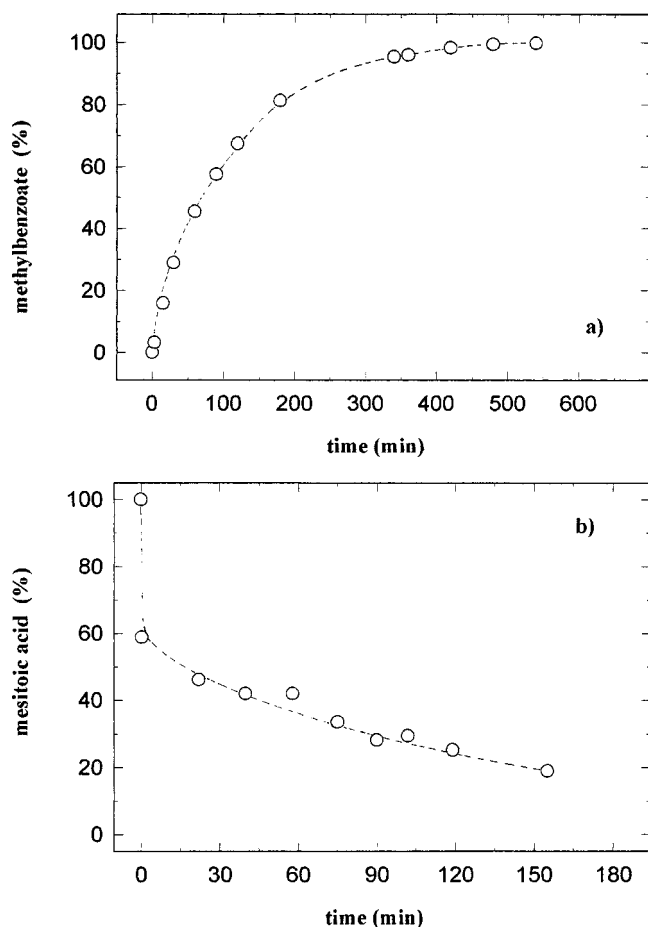


Figure 2. Esterification of benzoic and mesitoic acids with methanol in toluene over  $\text{H}_2\text{SO}_4/\text{SiO}_2$ . (a) Percentage of methyl benzoate vs. time (min) at  $60^\circ\text{C}$ . (Data by HPLC,  $[\text{ArCOOH}] = 0.54 \text{ mol dm}^{-3}$ , 4 g of catalyst =  $4.75 \text{ mmol H}_2\text{SO}_4 \text{ g}_{\text{catalyst}}^{-1}$ , ratio Ar:MeOH = 1:5.) (b) Mesitoic acid vs. time (min) at  $70^\circ\text{C}$ . (Data by GLC,  $[\text{mesitoic acid}] = 0.24 \text{ mol dm}^{-3}$ , 1 g of catalyst =  $4.64 \text{ mmol H}_2\text{SO}_4 \text{ g}_{\text{catalyst}}^{-1}$ , ratio Ar:MeOH = 1:5, volume of reaction = 10.6 ml.)

catalytic efficiency of these materials for obtaining methyl benzoate from benzoic acid and methanol (equilibrium (1)) is now tested using temperature, molar ratio of reagents, acid loading of catalysts given in table 1. Toluene has essentially been chosen as solvent, able to reduce drastically the catalytic deactivation due to methanol and water which are, for their limiting effect, the main unfavourable components of the system under investigation.

As concerns the performance of the catalysts it appears that all the samples can equally be used, as suggested by the following features: conversion and selectivity near 100 wt%, absence of by-products, short times of reaction between 50 and  $70^\circ\text{C}$ , catalysts easy to prepare, to handle and to store. From the results it also might be argued that the catalysts are suitable to avoid the phenomena of equilibrium and reversibility usually observed in aqueous acid solutions. For instance, selectivity, yield of products, differentiation between reagents and products in the adsorption phenomena suggest a high water adsorption power of the solid samples, suitable to shift the equilib-

rium of the reversible esterification towards high yields of esters.

In table 1 further experimental details related to kinetic behaviour of methyl benzoate at various times are reported. The trend of  $r_0$  values shows that temperatures of reaction and concentrations of reagents (i.e., ratio benzoic acid: methanol) are the parameters which are giving noteworthy variations of the reaction rates. Under these conditions, an apparent activation energy of ca.  $13.5 \text{ kcal mol}^{-1}$  has been estimated. In contrast, samples of catalysts dried at  $105^\circ\text{C}$  and at  $180^\circ\text{C}$  with different acid loadings, appear to be almost equally effective.

Attempts to understanding the catalytic performance of the samples with different acid loadings have also been made by using new parameters. For instance, by the  $k_a$  and  $k_b$  rate constants (or catalytic activity per proton) which are taking into account the loadings of the acid also corrected for the variation of surface area (SA) by a factor  $f$  (i.e.,  $k_a = r_0/[\text{acid}]$ ,  $k_b = r_0/[\text{acid}] \times f$ ,  $f = \text{SA}_{\text{cat}}/\text{SA}_{\text{SiO}_2}$ ).

All the results obtained are consistent between them and in agreement with the rate constants observed in aqueous acid solutions at a given temperature (see figure 3). Indeed, in the plots  $\log k_a$  vs. molarity of  $\text{H}_2\text{SO}_4$  linear rate profiles are observed whose intercepts, at  $-2.55$  for kinetic data in toluene at  $60^\circ\text{C}$  (or at  $-3.70$ , for kinetic data in methanol at  $25^\circ\text{C}$ ), are practically equal to the values observed for the esterification of benzoic acid with methanol carried out in MeOH + HCl (0.02 N) at the same temperature [37,38]. In the plots  $\log k_b$  vs. molarity of  $\text{H}_2\text{SO}_4$  it can be seen that the  $\log k_b$  values, within the limits of experimental errors, are independent of the acid loading of the catalysts and analogous to those observed in aqueous systems.

The kinetic trend of benzoic acid towards the esterification is consistent with the usual reaction scheme involving protonated benzoic acid ( $\text{ArC}(\text{OH})_2^+$ ) and methanol. However, the comparison of the results in liquid and solid phase also suggests that the acid strength requirements of the reaction are not very high. The behaviour of mono-substituted benzoic acids with *o*-, *m*-, *p*-activating or deactivating substituents as  $-\text{OMe}$ ,  $-\text{CH}_3$ ,  $-\text{F}$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{NO}_2$  support analogous conclusion. These compounds can be esterified in aqueous HCl (0.02–0.1 N) between 25 and  $60^\circ\text{C}$  and exhibit a low slope value (ca. 0.5) in the plot  $\log k$  (esterification) vs.  $\sigma$  ( $\sigma$  = Hammett substituent constants) [37,38].

Studies carried out over samples of  $\text{H}_2\text{SO}_4/\text{SiO}_2$  have also been attempted using mesitoic acid as substrate to be esterified. It allows one to test the catalytic performance of the solids by a reaction jointly controlled by two opposite factors: the requirement of a highly acid catalyst for obtaining the reacting species (i.e.,  $\text{MsCO}^+$  ion formed by the equilibrium (8)) and the limiting catalytic effect of methanol and water, intrinsic components of the system. The results obtained in toluene between 50 and  $70^\circ\text{C}$  show levels of conversion between 98 and 99 wt%, but a complex kinetic behaviour at short reaction time (see figure 2(b)). As concerns the selectivity, the amount of mesitylene ( $<1 \text{ wt}\%$ ) observed as by-product and related to decarboxylation of

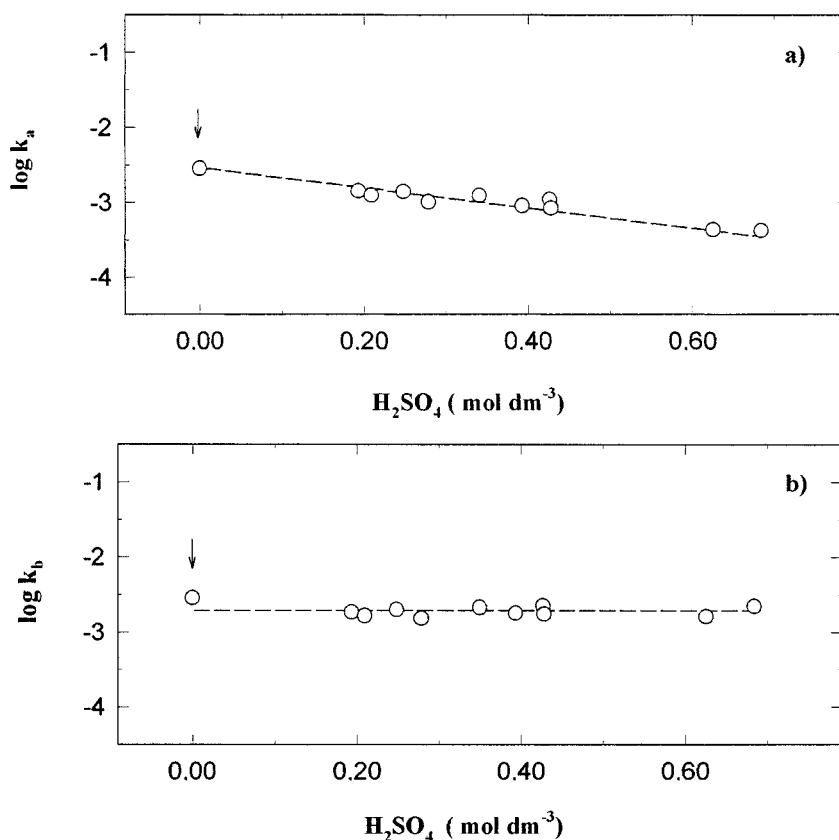


Figure 3. Esterification of benzoic acid with methanol in toluene over H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> at 60 °C. (a) log k<sub>a</sub> vs. molarity of H<sub>2</sub>SO<sub>4</sub> (log k<sub>a</sub> = log(r<sub>0</sub>/[acid])). (b) log k<sub>b</sub> vs. molarity of H<sub>2</sub>SO<sub>4</sub> (log k<sub>b</sub> = log(r<sub>0</sub>/[acid] × f) (f = SA<sub>cat</sub>/SA<sub>SiO<sub>2</sub></sub>)). (Experimental data in solid phase: present work, log k<sub>obs</sub> (↓) in CH<sub>3</sub>OH + HCl (0.02 N) from [37,38].)

mesitoic acid in strong acidic media [17], does not affect significantly the results.

From a practical point of view, these experimental observations suggest that the catalytic system under investigation can successfully be used in the esterification of carboxylic acids, whose reaction in aqueous systems can occur both by the species ArC(OH)<sub>2</sub><sup>+</sup> or by a positive acyl ion (i.e., 2,4,6-triMe-ArC=O<sup>+</sup>). It appears due to some attendant circumstance: (i) aprotic solvents, able to contain below 1% the loss of acid from the catalyst, (ii) selective adsorption-desorption equilibria of the chemical species, able to give high yields of products without water removal, and (iii) change in the catalytic performance of the solids in accordance to the reactivity of the reacting substrates.

From a point of view of acidity the chemical behaviours of benzoic and mesitoic acids appear to be determined by the concentrations and reactivities of the ions formed in the corresponding equilibrium process. The ArC(OH)<sub>2</sub><sup>+</sup> ion for instance, easily formed in the system by equilibrium (2) as unique reacting species, is of interest in the esterification of benzoic acid. One of the two ions, i.e., 2,4,6-triMe-ArC(OH)<sub>2</sub><sup>+</sup> and 2,4,6-triMe-ArC=O<sup>+</sup> characterized by different equilibria, different acidity ranges and different reactivities towards the esterification is, instead, of interest in the esterification of mesitoic acid. The complete conversion of mesitoic acid to the corresponding ester over

H<sub>2</sub>SO<sub>4</sub>/SiO<sub>2</sub> is therefore consistent with acidic media able to give mesitoyl cation being, between the reactive species, the only one that can be converted to the product. In aqueous solution, acidity ranges between 92 and 98 wt% H<sub>2</sub>SO<sub>4</sub> are occurring for an analogous reaction.

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