

# On the acidity of liquid and solid acid catalysts.

## Part 2. A thermodynamic and kinetic study for acid-catalysed nitrations

Nunziata Clara Marziano<sup>a,\*</sup>, Claudio Tortato<sup>a</sup>, Lucio Ronchin<sup>a</sup>, Federica Martini<sup>a</sup> and Claudia Bianchi<sup>b</sup>

<sup>a</sup> *INFN and Chemistry Department, University of Venice, Dorsò Duro 2137, 30123 Venice, Italy*

<sup>b</sup> *Department of Physical Chemistry and Electrochemistry, University of Milan, Golgi 19, 20133 Milan, Italy*

Received 1 December 1998; accepted 12 February 1999

Solid acids prepared by adding sulfuric acid on silica gel have been used as catalysts in the nitration of nitrobenzenes and their properties have been tested by kinetic studies at 25 °C. Nitration rates in concentrated aqueous solutions of sulfuric acid were also analysed and the catalytic efficiencies of sulfuric acid in liquid and solid phase were compared by using kinetic data of analogous compounds. The results show that the solid acid samples exhibit nitrating properties very similar to those observed in concentrated aqueous solutions of sulfuric acid (range of 90 wt%). The relationship between nitration rates and effective concentration of electrophilic species  $[\text{NO}_2^+]$ , determined by studying the protonation–dehydration equilibrium of nitric acid in strong acids ( $\text{HNO}_3 + \text{H}^+ \rightleftharpoons \text{H}_2\text{O} + \text{NO}_2^+$ ), was tested to better understand the acidity properties of medium.

**Keywords:** nitration, sulfuric acid, solid acid catalysts

### 1. Introduction

Acid-catalysed reactions over solid acids are the subject of continuous studies in the attempt to develop new procedures in the catalytic processes of bulk and fine chemicals [1–3]. Simplification in handling techniques and environmental protection are also reasons of interest in this field since selected acid materials would have the advantages of decreasing corrosion, by-products and further unfavourable aspects associated with the use of concentrated aqueous acid solutions in catalysis.

In the present paper, acid catalysts made of sulfuric acid supported on silica gel are tested, using the nitration process of aromatic compounds and the nitration rates of analogous compounds which are measured both in solid acid samples and in concentrated aqueous solution of sulfuric acid. This approach allows one to study the catalytic properties of the materials under investigation and to compare the catalytic efficiency of sulfuric acid in liquid and in solid phase by a well known reaction [4–6] where “the acidity” of the medium is the key parameter to be determined for the conversion reagents  $\rightarrow$  products.

### 2. Experimental

#### 2.1. Materials

Samples of commercially available GRACE GmbH Silica Gel (90  $\mu\text{m}$  average particle size, 390  $\text{m}^2/\text{g}$  ( $S_{\text{BET}}$ ),

1.14 ml/g pore volume) were used. Purified silica gel samples were obtained by washing the material with aqueous solutions of perchloric acid, then with distilled water.

Purified aromatic substrates (4-chloro-3-nitrotoluene, nitrobenzene, *o*-, *m*-, *p*-chloronitrobenzenes) and solvent (dichloromethane) were obtained from the commercially available products. Nitric acid was purified by vacuum distillation from concentrated sulfuric acid and was stored at  $-50$  °C. Aqueous sulfuric acid solutions of various strengths were prepared by diluting the concentrated acid (Analar grade) and their percentage compositions were determined by automatic potentiometric titrations against standard solutions of NaOH. Nitric acid and aromatic solutions in dichloromethane were prepared by weighing both reagent and solvent.

#### 2.2. Solid acid samples

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 °C in a stream of  $\text{N}_2$ . The acid percentage composition in the solids was measured by automatic potentiometric titrations against standard solutions of NaOH. The surface areas of the samples show a continuous decrease as the amount of sulfuric acid adsorbed by the solid increases. The observed values are between 247 and 108  $\text{m}^2/\text{g}$  for acid samples with loadings between 3.31 and 5.07 mmol  $\text{H}_2\text{SO}_4/\text{g}_{\text{catalyst}}$ .

\* To whom correspondence should be addressed.

Table 1  
Second-order rate constants in solid ( $k_{2\text{obs}}$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ))<sup>a</sup> and in aqueous sulfuric acid ( $k_2^0$  ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ))<sup>b</sup> for acid-catalysed nitrations of aromatic compounds at 25 °C.

	log $k_{2\text{obs}}$ (solid) at <sup>a</sup>							log $k_2^0$ (solution) <sup>b</sup>
	1.93	3.15	3.31	4.15	4.25	5.00	5.07	
4-chloro-3-nitrotoluene				-0.55				0.15
<i>o</i> -chloronitrobenzene	-0.65	-0.98	-0.96	-1.08	-1.12	-1.21	-1.25	-0.60
Nitrobenzene	-1.13		-1.42	-1.37			-1.55	-1.10
<i>m</i> -chloronitrobenzene				-1.85				-1.75
<i>p</i> -chloronitrobenzene				-2.16				-2.10

<sup>a</sup> Values estimated in solid catalysts ( $\text{H}_2\text{SO}_4/\text{SiO}_2$ ) by using the stoichiometric concentration of solutes (rate =  $k_{2\text{obs}} \times [\text{Ar}]_{\text{st.}}[\text{HNO}_3]_{\text{st.}}$ ). Samples with 1.93, 3.15, 3.31, 4.15, 4.25, 5.00, and 5.07 mmol  $\text{H}_2\text{SO}_4/\text{g}_{\text{catalyst}}$ .

<sup>b</sup> Values estimated in concentrated aqueous sulfuric (range < 90 wt%) acid by using the effective concentration of solutes (rate =  $k_2^0[\text{Ar}][\text{NO}_2^+]$ ). The  $k_2^0$  of benzene = 6.05 [9].

### 2.3. Kinetic measurements in aqueous acid solutions

Separate solutions of aromatic and nitric acid in sulfuric acid of appropriate concentration were prepared using weighed samples of solvent and reagents. A small volume of the aromatic solution was transferred by micrometric syringe to an optical cell containing a weighed sample of nitric acid in sulfuric acid. The cell was kept at 25 °C by a digital thermostat and the change of absorbance with time at selected wavelengths was followed. As observed in aqueous acid solutions [4–9], second-order kinetics were found to hold and rate coefficients ( $k_{2\text{obs}}$  ( $\text{dm}^{-3} \text{mol}^{-1} \text{s}^{-1}$ )) related to stoichiometric concentrations of reagents (rate =  $k_{2\text{obs}}[\text{Ar}]_{\text{st.}}[\text{HNO}_3]_{\text{st.}}$ ) were determined, using either excess nitric acid ( $[\text{HNO}_3] 10^{-3}$ – $10^{-2} \text{mol dm}^{-3}$ ,  $[\text{Ar}] 10^{-4}$ – $10^{-5} \text{mol dm}^{-3}$ ) or equimolar concentrations of nitric acid and aromatic ( $[\text{HNO}_3]$  and  $[\text{Ar}] 10^{-3}$ – $10^{-2} \text{mol dm}^{-3}$ ).

The rate constants for 4-chloro-3-nitrotoluene (*A*) and *m*-chloronitrobenzene (*B*), not available in literature and obtained at a given percentage of sulfuric acid, are:

$$\begin{aligned} \log k_{2\text{obs}} \text{ of } A & \\ &= -1.439 \text{ (at 83.72 wt\%), } -1.476 \text{ (at 83.87 wt\%),} \\ &\quad -0.623 \text{ (at 86.08 wt\%), } -0.185 \text{ (at 88.23 wt\%),} \\ &\quad 0.125 \text{ (at 90.25 wt\%), } -0.148 \text{ (at 93.25 wt\%),} \\ &\quad -0.228 \text{ (at 93.95 wt\%), } -0.301 \text{ (at 94.52 wt\%),} \\ &\quad -0.62 \text{ (at 96.13 wt\%);} \end{aligned}$$

$$\begin{aligned} \log k_{2\text{obs}} \text{ of } B & \\ &= -2.616 \text{ (at 85.89 wt\%), } -2.268 \text{ (at 86.90 wt\%),} \\ &\quad -2.228 \text{ (at 87.15 wt\%), } -1.796 \text{ (at 90.02 wt\%),} \\ &\quad -1.808 \text{ (at 90.02 wt\%), } -1.830 \text{ (at 91.93 wt\%),} \\ &\quad -1.810 \text{ (at 91.93 wt\%), } -2.085 \text{ (at 96.16 wt\%),} \\ &\quad -2.376 \text{ (at 98.66 wt\%).} \end{aligned}$$

### 2.4. Kinetic measurements in solid acid catalysts

Separate solutions of aromatic and nitric acid in dichloromethane of appropriate concentration were prepared using weighed samples of solvent and reagents. A small volume

of the aromatic solution was transferred by micrometric syringe in a well stirred UV cell containing weighed samples of the catalyst and nitric acid in dichloromethane. In this case, the incoming beam was focused on the sample at a proper height and care was taken to avoid local turbulences. The cell was kept at 25 °C and the kinetic runs were performed under the experimental details described above. As in aqueous acid solutions, second-order kinetics were found to hold for nitration of 4-chloro-3-nitrotoluene, nitrobenzene and *o*-, *m*-, *p*-chloronitrobenzenes, using acid samples with 1.93, 3.31, 4.15, and 5.07 mmol  $\text{H}_2\text{SO}_4/\text{g}_{\text{catalyst}}$ .

The rate coefficients ( $k_{2\text{obs}}$ ) observed for the compounds under investigation are reported in table 1.

An inspection of the Carberry and Weeler–Weisz number for the nitration of chlorobenzene, the latter one used to test fast reactions, allows one to state that both liquid/solid and internal pore diffusion do not affect the overall reaction kinetics. The calculated values for Carberry and Weeler–Weisz number are ca.  $10^{-3}$  and  $10^{-2}$ , respectively [10].

### 2.5. XPS and equilibria measurements in solid acid catalysts

The surface layer of the solid acid samples has been characterized by XPS measurements using pyridine chemisorption [11] and investigation of the  $\text{N}_{1s}$  XPS band. A single peak at 401.4 eV was found in all cases, highlighting only the presence of rather strong Brønsted acid sites.

The binding energy (BE) of  $\text{N}_{1s}$ ,  $\text{Si}_{2p}$ ,  $\text{S}_{2p}$  was also measured for a catalyst containing 2.52 mmol  $\text{H}_2\text{SO}_4/\text{g}_{\text{catalyst}}$  and different amounts of adsorbed isopropyl nitrate. The latter was used as the precursor of the effective nitrating agent ( $\text{NO}_2^+$ ). The results show a linear relationship on the plots  $\text{Si}/\text{N}$  and  $\text{S}/\text{N}$  vs. the amount of the nitrating agent added to the sample.

Additional measurements related to protonating ability of the catalysts in the ( $\text{B} + \text{H}^+ \rightleftharpoons \text{BH}^+$ ) process were performed in a thin UV cell (0.1 cm) filled with the solid acid + solvent + B and subjected to centrifugation. 3-methyl-2,4,6-trinitroaniline, 3-bromo-2,4,6-trinitroaniline, 2,4,6-trinitroaniline (TNA) were used as indicators (B).

These compounds are very weak bases and their half protonation in aqueous solutions of sulfuric acid occurs at

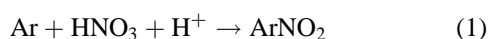
85.5, 92.8, 96.4 wt% H<sub>2</sub>SO<sub>4</sub>, respectively [12–17], with an order 3Me > 3Br > H, different from that expected according to the relationship between basic strength and substituent effects. The results in solids show an analogous trend, since the protonation can be easily observed for 3-methyl-TNA but not for the unsubstituted TNA. The behaviour of 3-Br-TNA is between them.

It appears to be a complication of the liquid and solid systems with sulfuric acid. Indeed, the order 3Me > H > 3Br was found in concentrated aqueous CF<sub>3</sub>SO<sub>3</sub>H by protonation studies of weak bases in this acid [18].

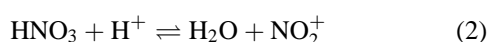
### 3. Results and discussion

#### 3.1. Nitration of aromatic compounds in aqueous sulfuric acid

Nitric acid in concentrated aqueous solutions of HClO<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H and H<sub>2</sub>SO<sub>4</sub> is known to be a good nitrating system for aromatic compounds (equilibrium (1)) [4–9]:



because of the catalytic efficiency of the medium for the formation of nitronium ion (equilibrium (2)) which is recognised as the actual nitrating agent [4–6,19–22]:



From a practical point of view, aqueous sulfuric acid between 50 and 100 wt% is the most commonly used solvent, suitable for nitration of substrates with very different reactivity such as mesitylene and nitrobenzenes [4–6,8,9]. The acidity dependence of nitration rates ( $k_{2\text{obs}}$ ) of some activated and deactivated aromatic compounds (Ar), related to stoichiometric concentration of reagents by equation (3) is shown in figure 1(A):

$$\text{rate} = k_{2\text{obs}}[\text{Ar}]_{\text{st.}}[\text{HNO}_3]_{\text{st.}} \quad (3)$$

The trend of rate profiles suggests two main observations: a steep increase up to a maximum in going from dilute solutions to 90 wt% acid and a gentle decrease in 90–100 wt% H<sub>2</sub>SO<sub>4</sub>, where the nitric acid is completely converted into NO<sub>2</sub><sup>+</sup> [4–6,9,19–21]. A similar dependence of the rate profiles upon acidity was found in the nitration studies of aromatic compounds in the range 60–100 wt% CF<sub>3</sub>SO<sub>3</sub>H [7].

Besides the conventional description using  $k_{2\text{obs}}$ , the nitration process can be analysed on the basis of the “ $k_2^0$ ” rate constants [7–9,22], the latter ones being estimated in connection with the effective concentration of solutes (equation (4)):

$$\text{rate} = k_2^0[\text{Ar}][\text{NO}_2^+] \quad (4)$$

The  $k_{2\text{obs}}$  and  $k_2^0$  rate constants are related by

$$k_{2\text{obs}}[\text{Ar}]_{\text{st.}}[\text{HNO}_3]_{\text{st.}} = k_2^0[\text{Ar}][\text{NO}_2^+] \quad (5)$$

The new parameters are of interest being new sources of information that allow the separation of solvent effects involved in the equilibria of reagents from solvent effects

involved on the kinetic behaviour of the reacting species. Indeed, in the range below 90 wt% H<sub>2</sub>SO<sub>4</sub>, the  $k_2^0$  values obtained by taking into account the actual concentrations of NO<sub>2</sub><sup>+</sup> were found to be practically independent of medium acidity (see figure 1(B)). In the range 89–91%, where [HNO<sub>3</sub>]<sub>st.</sub> ≈ [NO<sub>2</sub><sup>+</sup>], the condition  $k_{2\text{obs}} \approx k_2^0$  is satisfied. The results of this study, which has been extended to a much larger number of substrates in different acids, suggest a number of items for discussion: (i) The different behaviour of  $k_{2\text{obs}}$  and  $k_2^0$  shows that the change in  $k_{2\text{obs}}$  arises essentially from the change in the position of HNO<sub>3</sub> → NO<sub>2</sub><sup>+</sup> equilibrium. (ii) Estimated  $k_2^0$  values are almost the same in HClO<sub>4</sub>, CF<sub>3</sub>SO<sub>3</sub>H, H<sub>2</sub>SO<sub>4</sub> for all the substrates already studied. (iii) Interactions between ions giving HSO<sub>4</sub><sup>−</sup>NO<sub>2</sub><sup>+</sup> ion pairs have been suggested above 90 wt% [7–9,22]. The kinetic dependence on temperature supports the involvement of analogous species since, only in this range, the decreasing factor of rates becomes smaller when the temperature rises.

The determination of the  $k_2^0$  rate coefficients necessarily requires the knowledge of [NO<sub>2</sub><sup>+</sup>], the latter obtained according to Raman, UV and NMR studies of equilibrium (2) in H<sub>2</sub>SO<sub>4</sub> between 82 and 92 wt% H<sub>2</sub>SO<sub>4</sub> [19–21]. Outside this range experimentally available for the measurements, the [NO<sub>2</sub><sup>+</sup>] was estimated by a procedure suitable for solutes protonating in non-ideal acid solutions [33–37]. For instance, the equilibrium constant ( $pK_{\text{NO}_2^+}$ ) and the acidic dependence of [NO<sub>2</sub><sup>+</sup>] in H<sub>2</sub>SO<sub>4</sub> have been determined by equation (6), rewritten as (6'), where the Mc(i) function or “activity coefficient function” – defined formally by equation (7) – takes into account the variation of activity coefficient (a.c.) term of the species involved in the process:

$$pK_{\text{NO}_2^+} = \log \left\{ \frac{[\text{NO}_2^+][\text{H}_2\text{O}]}{[\text{HNO}_3][\text{H}^+]} - \log \left( \frac{f_{\text{HNO}_3} f_{\text{H}^+}}{f_{\text{NO}_2^+} f_{\text{H}_2\text{O}}} \right) \right\} \quad (6)$$

$$pK_{\text{NO}_2^+} = \log \left\{ \frac{[\text{NO}_2^+][\text{H}_2\text{O}]}{[\text{HNO}_3][\text{H}^+]} + n_{\text{NO}_2^+} \text{Mc}(i) \right\} \quad (6')$$

$$\text{Mc}(i) = \log (\text{product of reactants' a.c.}) - \log (\text{product of products' a.c.}) \quad (7)$$

Furthermore, studies related both to protonation equilibria of weak bases (B) (B + H<sup>+</sup> ⇌ BH<sup>+</sup>) in concentrated aqueous acid solutions (HA) (for HA = HCl, HBr, HNO<sub>3</sub>, HClO<sub>4</sub>, CH<sub>3</sub>SO<sub>3</sub>H, CF<sub>3</sub>SO<sub>3</sub>H, H<sub>2</sub>SO<sub>4</sub>) and to dissociation equilibria of HA itself (HA ⇌ H<sup>+</sup> + A<sup>−</sup>), show the validity of the relationships (8) or (8') between solutes (i) and solvents (s):

$$\text{Mc}(i) = n_{\text{is}} \text{Mc}(s), \quad (8)$$

$$-\log(f_{\text{B}} f_{\text{H}^+} / f_{\text{BH}^+}) = -n_{\text{is}} \log(f_{\text{A}^-} f_{\text{H}^+} / f_{\text{HA}}) \quad (8')$$

It suggests that the deviation from ideality (determined by the Mc a.c. function) and the interactions between solutes and solvents (determined by the  $n$  values) are the parameters to be taken into account when equilibria and rates in

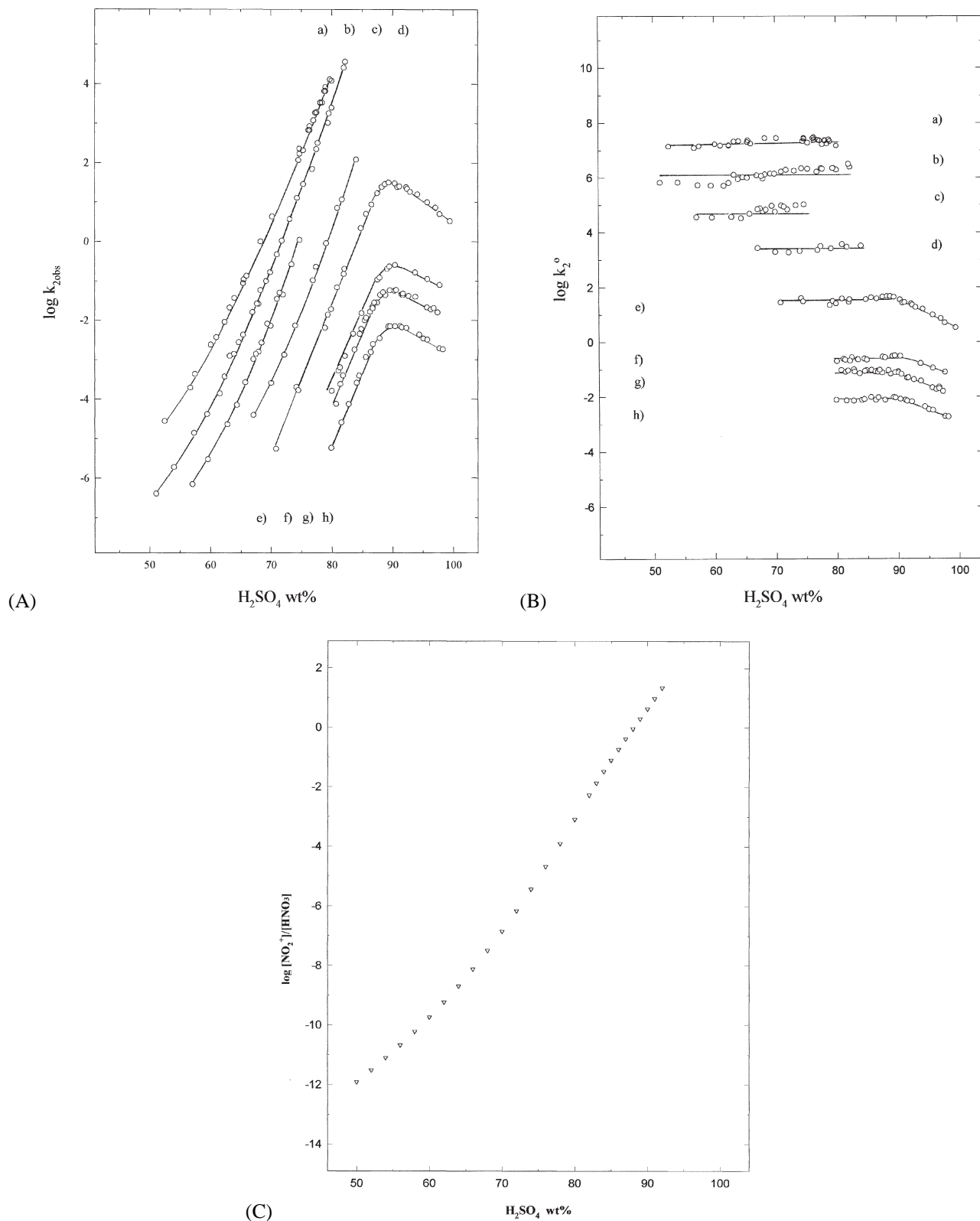


Figure 1. (A) Nitration in aqueous sulfuric acid at 25 °C. Values of  $\log k_{2,obs}$  vs. wt%  $H_2SO_4$ . (a) Toluene, (b) benzene, (c) bromobenzene, (d) *p,p'*-dibromobenzene, (e) *p*-nitrotoluene, (f) *o*-Cl-nitrobenzene, (g) nitrobenzene, (h) *p*-Cl-nitrobenzene (experimental data of: (a) from [23–26], (b) from [23,27,28], (c) from [27–29], (d) from [29], (e) from [31], (f) from [31], (g) from [32], (h) from [31]). (B) Nitration in aqueous sulfuric acid at 25 °C. Values  $\log k_2^0$  vs. wt%  $H_2SO_4$ . (a) Toluene, (b) benzene, (c) bromobenzene, (d) *p,p'*-dibromobenzene, (e) *p*-nitrotoluene, (f) *o*-Cl-nitrobenzene, (g) nitrobenzene, (h) *p*-Cl-nitrobenzene (experimental data as in figure 1(A)). (C) Protonation–dehydration equilibrium of nitric acid in aqueous sulfuric acid. Values of  $\log [NO_2^+]/[HNO_3]$  at 25 °C: range 50–82 wt%  $H_2SO_4$ , estimated values; range 85–92 wt%  $H_2SO_4$ , experimental data from [21].

strong acids are analysed. The  $n$  values, in particular, have been interpreted as a measure of the specific interactions between solutes and solvents in the proton transfer process  $\text{H}_3\text{O}^+\text{A}^- \rightarrow \text{BH}^+\text{A}^-$  [9,18,36,37].

The parameters of equilibrium (2) that have been found at 25 °C according to equation (6') are:  $\text{p}K_{\text{NO}_2^+} = -17.3$ ,  $n_{\text{NO}_2^+} = 2.46$  (in  $\text{H}_2\text{SO}_4$ ) [9]. The values are related, respectively, to intercept ( $\text{p}K_{\text{NO}_2^+}$ ) and slope ( $n_{\text{NO}_2^+}$ ) of the plot

$$\log \left\{ \frac{[\text{NO}_2^+][\text{H}_2\text{O}]}{[\text{HNO}_3][\text{H}^+]} \right\} = \log V_N$$

vs. the Mc(i).

Analogous studies of  $[\text{NO}_2^+]/[\text{HNO}_3]$  ratios in  $\text{CF}_3\text{SO}_3\text{H}$  at 25 °C support the validity of the  $\text{p}K_{\text{NO}_2^+}$  value, being  $\text{p}K_{\text{NO}_2^+} = -17.3$  and  $n_{\text{NO}_2^+} = 3.37$  the parameters estimated in this acid by using the corresponding  $\log V_N$  and Mc values at the defined temperature [9].

In figure 1(C), the solvent dependence of  $\log [\text{NO}_2^+]/[\text{HNO}_3]$  ratio is reported. In the range 50–80 wt%  $\text{H}_2\text{SO}_4$ , changes of  $\log [\text{NO}_2^+]/[\text{HNO}_3]$  between  $10^{-12}$  and  $10^{-2}$  were estimated, according to the  $k_{2\text{obs}}$  rate profiles of nitration [9] (see figure 1(A)).

### 3.2. Nitration of aromatic compounds in solid acid catalysts

Preliminary studies related to nitration of aromatic compounds over  $\text{H}_2\text{SO}_4/\text{SiO}_2$  have shown that these materials can be successfully used as catalysts to obtain reaction products [38]. The main experimental observations of practical interest are: The performance of the solids can be easily modified in accordance to the reactivity of the aromatic substrates. The catalysts can be prepared from inexpensive materials and oven reactivated for further use with a minimal loss of catalytic efficiency. Good yields of nitrocompounds (>95%) are obtained at 25 °C for aromatic compounds with different reactivities. Experimental tests with isopropyl nitrate as nitrating agent confirm that the nitration takes place on the catalyst.

An extension of these studies by kinetic investigations is now reported using purified nitric acid as nitrating agent, nitrobenzene and substituted nitrobenzenes as aromatic compounds and samples of  $\text{H}_2\text{SO}_4/\text{SiO}_2$  (with added sulfuric acid between 2 and 5 mmol acid/g<sub>catalyst</sub>) as catalysts. For nitrations in aqueous acid solutions, the selected compounds require acidity ranges between 80 and 100 wt%  $\text{H}_2\text{SO}_4$  being less reactive than benzene by a factor between  $10^6$  and  $10^9$  (see figure 1(B)). Examples of the observed rate constants ( $k_{2\text{obs}}$ ) determined by equation (3) are reported in table 1.

The new experimental observations reveal some significant points:

- (i) There is, now, kinetic evidence that the  $\text{H}_2\text{SO}_4/\text{SiO}_2$  catalysts exhibit catalytic properties analogous to those observed in concentrated aqueous sulfuric acid (range of 90 wt%).

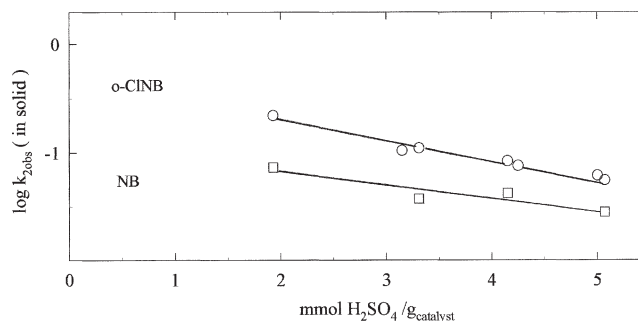


Figure 2. Nitration rates of *o*-chloronitrobenzene and nitrobenzene in solid acid catalyst. Values of  $\log k_{2\text{obs}}$  vs. mmol  $\text{H}_2\text{SO}_4/\text{g}_{\text{catalyst}}$  (experimental data – present work).

- (ii) The observed rate constants ( $k_{2\text{obs}}$ ) were found to be linearly related to parameter  $X$  (where  $X = [\text{catalyst}](\text{mmol H}_2\text{SO}_4/\text{g}_{\text{catalyst}})/[\text{HNO}_3]$ ). The variations, however, for *o*-chloronitrobenzene and nitrobenzene are found to be very small using  $[\text{HNO}_3]$  between  $5 \times 10^{-3}$  and  $3 \times 10^{-2}$  M and acid samples with 3.31 and 5.07 mmol acid/g<sub>catalyst</sub>.
- (iii) The nitration rates of *o*-chloronitrobenzene and nitrobenzene and their variations with mmol acid/g<sub>catalyst</sub> are depicted in figure 2. The trend appears to be analogous to that observed in aqueous sulfuric acid above 90 wt% (see figure 1) since the “acidity” of the catalysts does not affect significantly the nitration rates, as expected for medium compositions where the ionization of  $\text{HNO}_3$  to  $\text{NO}_2^+$  is virtually complete. In contrast, the solvent dependence of  $k_{2\text{obs}}$  is usually very large in the range where the position of  $\text{HNO}_3$ – $\text{NO}_2^+$  equilibrium is changed. For instance, between 50 and 80 wt%  $\text{H}_2\text{SO}_4$  the rate of anisole nitration increases by a factor of  $10^{12}$  and between 80 and 90 wt%  $\text{H}_2\text{SO}_4$  the rate of nitrobenzenes nitration increases by a factor of  $10^3$ . Further experimental observations involved with the decreasing slopes of figure 2, with the differences between  $k_{2\text{obs}}$  and  $k_2^0$  for nitrating compounds with a progressive increase in the reactivity (see table 1) and with the high protonating ability of the catalysts (see section 2), necessarily suggest that also the process  $\text{B} \rightarrow \text{BH}^+$  of nitrobenzenes cannot be neglected in proportion to their basic strength [18].
- (iv) Of particular interest are the results obtained by comparing the reaction rates of analogous compounds in liquid (aqueous  $\text{H}_2\text{SO}_4$ ) and in solid ( $\text{H}_2\text{SO}_4/\text{SiO}_2$ ) phase (see figure 3(a)). Within the limits of experimental uncertainty, the relative rate constants ( $k_{2\text{obs}}(\text{X-PhNO}_2)/k_{2\text{obs}}(\text{PhNO}_2)$ ) of 3-chloro-4-nitrotoluene, nitrobenzene, *o*-, *m*-, *p*-chloronitrobenzenes obtained in both phases are found to be linearly related between them.

A similar trend has already been observed by comparing nitration rates of analogous compounds in aqueous acid media and in the gas phase [7]. In figure 3(b),

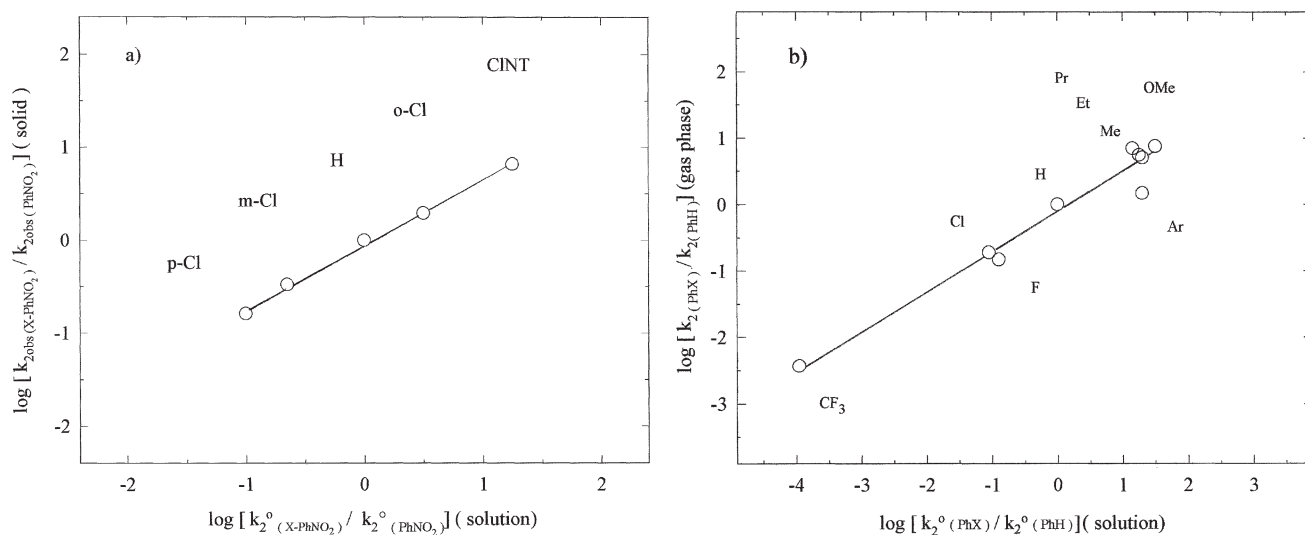


Figure 3. (a) Values of  $\log[k_{2\text{obs}}(\text{X-PhNO}_2)/k_{2\text{obs}}(\text{PhNO}_2)]$  (solid-phase nitration) vs.  $\log[k_2^0(\text{X-PhNO}_2)/k_2^0(\text{PhNO}_2)]$  (nitration in aqueous  $\text{H}_2\text{SO}_4$ ) of nitrocompounds: *p*-chloronitrobenzene (*p*-CINB); *m*-chloronitrobenzene (*m*-CINB); nitrobenzene (NB); *o*-chloronitrobenzene (*o*-CINB); *p*-chloro-*m*-nitrotoluene (CINT) (experimental data in solid phase – present work; in liquid phase, (*m*-CINB) and (CLNT) – present work, (*p*-CLNB) from [31], (NB) from [32]). (b) Values of  $\log[k_2(\text{PhX})/k_2(\text{PhH})]$  (gas-phase nitration) vs.  $\log[k_2^0(\text{PhX})/k_2^0(\text{PhH})]$  (nitration in aqueous  $\text{H}_2\text{SO}_4$ ) of monosubstituted arenes: anisole (OMe); toluene (Me); ethylbenzene (Et); propylbenzene (Pr); biphenyl (Ar); benzene (H); fluorobenzene (F); chlorobenzene (Cl); benzotrifluoride (CF<sub>3</sub>) (experimental data in gas phase from [39]; in  $\text{H}_2\text{SO}_4$  from [7]).

for instance,  $k_{2(\text{PhX})}^0/k_{2(\text{PhH})}^0$  values obtained in aqueous  $\text{H}_2\text{SO}_4$  and  $k_{(\text{PhX})}/k_{(\text{PhH})}$  values obtained in the gas phase were compared using the experimental data of aromatics available in both phases [7,39].

- (v) From a practical point of view all the results show that activated and deactivated aromatics such as mesitylene and *p*-chloronitrobenzene, whose reactivities differ by a factor of  $10^{11}$ , can be easily nitrated at  $25^\circ\text{C}$  over  $\text{H}_2\text{SO}_4/\text{SiO}_2$  solid acids.

The high catalytic property of the materials observed in the nitration is in agreement with their high protonating ability, the latter one observed in the protonation process of nitroanilines, carried out in  $\text{HClO}_4/\text{SiO}_2$ ,  $\text{CF}_3\text{SO}_3\text{H}/\text{SiO}_2$  and  $\text{H}_2\text{SO}_4/\text{SiO}_2$  [40–42]. In these studies it has been shown that equation (8) or (8') holds for the acid materials under investigation. Moreover, for analogous compounds, the protonating ability (or  $n$  value) of  $\text{HClO}_4$ ,  $\text{CF}_3\text{SO}_3\text{H}$  and  $\text{H}_2\text{SO}_4$  in liquid and solid phase differ by a factor of ca.  $10^4$ – $10^5$ , but the thermodynamic  $\text{p}K_{\text{BH}^+}$  values of  $B$  in both systems are found to be the same.

The  $\text{H}_2\text{SO}_4/\text{SiO}_2$  catalysts were also found to be more active than other ones already tested for nitration. Nafion-H, for instance, allows the nitration of benzene by heating the reaction mixture to reflux [43], and mordenite by heating at  $170^\circ\text{C}$  [44]. Zeolite beta at  $25^\circ\text{C}$  allows the nitration of moderately activated substrates [45].

#### 4. Conclusion

For acid-catalysed nitration of nitrobenzenes it was shown that the catalytic efficiency of solid acids prepared by wet impregnation of  $\text{H}_2\text{SO}_4$  to silica gel and with

2–5 mmol acid/g<sub>catalyst</sub> can be compared to that observed in very concentrated aqueous  $\text{H}_2\text{SO}_4$  (range 90 wt%). In this particular range of acid solutions, where the ionization of  $\text{HNO}_3$  to  $\text{NO}_2^+$  is virtually complete, the nitration rates related to the stoichiometric concentration of nitric acid (rate =  $k_{2\text{obs}}[\text{Ar}]_{\text{st.}}[\text{HNO}_3]_{\text{st.}}$ ) are very near to the rates related to the effective concentration of electrophilic species (rate =  $k_2^0[\text{Ar}][\text{NO}_2^+]$ ). The kinetic results in solid were found to be consistent with those obtained by thermodynamic studies where the high protonating ability of the materials, compared to that observed in aqueous acid solutions, was shown.

It can be concluded that comparative studies in liquid and in solid phase and the description of “acidity” by suitable parameters with a thermodynamic significance can be useful tools for understanding the catalytic performance and the acid strength of complex acid systems.

#### References

- [1] K. Tanabe, H. Hattori, T. Yamaguchi and T. Tanaka, *Acid-Base Catalysis* (VCH, New York, 1989).
- [2] A. Corma, *Chem. Rev.* 95 (1995) 559.
- [3] A. Corma and H. Garcia, *Catal. Today* 38 (1997) 257.
- [4] M. Liler, *Reaction Mechanisms in Sulphuric Acid* (Academic Press, London, 1971).
- [5] K. Schofield, *Aromatic Nitration* (Cambridge University Press, Cambridge, 1980).
- [6] G.A. Olah, R. Malhotra and S.C. Narang, *Nitration. Methods and Mechanisms* (VCH, New York, 1989).
- [7] N.C. Marziano, C. Tortato and M. Sampoli, *J. Chem. Soc. Perkin Trans. 2* (1991) 423.
- [8] N.C. Marziano, A. Tomasin and C. Tortato, *J. Chem. Soc. Perkin Trans. 2* (1991) 1575.
- [9] N.C. Marziano, A. Tomasin, C. Tortato and J.M. Zaldivar, *J. Chem. Soc. Perkin Trans. 2* (1998) 1973.

- [10] J.J. Carberry, *Catal. Sci. Technol.* 8 (1987) 131.
- [11] R.B. Borade, A. Adnot and S. Kaliaguine, *J. Catal.* 126 (1990) 6.
- [12] L.P. Hammett and A.J. Deyrup, *J. Am. Chem. Soc.* 54 (1932) 2721.
- [13] M.J. Jorgenson and D.R. Hartter, *J. Am. Chem. Soc.* 85 (1963) 878.
- [14] M.I. Vinnik and R.S. Ryabova, *Russ. J. Phys. Chem.* 38 (1964) 320.
- [15] C.D. Johnson, A.R. Katritzky and S.A. Shapiro, *J. Am. Chem. Soc.* 91 (1969) 6654.
- [16] P. Tikle, A.G. Briggs and J.M. Wilson, *J. Chem. Soc. B* (1970) 65.
- [17] R.J. Gillespie, J.E. Peel and E.A. Robinson, *J. Am. Chem. Soc.* 93 (1971) 5083.
- [18] N.C. Marziano, A. Tomasin, C. Tortato and P. Isandelli, *J. Chem. Soc. Perkin Trans. 2* (1998) 2535.
- [19] N.C. Marziano, P. Traverso, A. De Santis and M. Sampoli, *J. Chem. Soc. Chem. Commun.* (1978) 873.
- [20] D.S. Ross, K.F. Kulmann and R.J. Malhotra, *J. Am. Chem. Soc.* 105 (1983) 4299.
- [21] M. Sampoli, A. De Santis, N.C. Marziano, F. Pinna and A. Zingales, *J. Phys. Chem.* 89 (1985) 2864.
- [22] N.C. Marziano, A. Tomasin and M. Sampoli, *J. Chem. Soc. Perkin Trans. 2* (1991) 1995.
- [23] R.G. Coombes, R.B. Moodie and K. Schofield, *J. Chem. Soc. B* (1968) 800.
- [24] J.W. Chapman and A.N. Strachan, *J. Chem. Soc. Chem. Commun.* (1974) 293.
- [25] J.W. Barnett, R.B. Moodie, K. Schofield and J.B. Weston, *J. Chem. Soc. Perkin Trans. 2* (1975) 648.
- [26] R.B. Moodie, K. Schofield and P.G. Taylor, *J. Chem. Soc. Perkin Trans. 2* (1979) 133.
- [27] N.C. Deno and R. Stein, *J. Am. Chem. Soc.* 78 (1956) 578.
- [28] N.C. Marziano, A. Zingales and V. Ferlito, *J. Org. Chem.* 42 (1977) 2511.
- [29] R.G. Coombes, D.H. Crout, J.G. Hoggett, R.B. Moodie and K. Schofield, *J. Chem. Soc. Perkin Trans. 2* (1970) 347.
- [30] R.B. Moodie, K. Schofield and J.B. Weston, *J. Chem. Soc. Perkin Trans. 2* (1976) 1089.
- [31] M.I. Vinnik, Zh. Grabovskaya and L.N. Arzameskova, *Russ. J. Phys. Chem.* 41 (1967) 580.
- [32] N.C. Marziano, M. Sampoli, F. Pinna and A. Passerini, *J. Chem. Soc. Perkin Trans. 2* (1984) 1163.
- [33] N.C. Marziano, G. Cimino and R. Passerini, *J. Chem. Soc. Perkin Trans. 2* (1973) 1915.
- [34] N.C. Marziano, P. Traverso, A. Tomasin and R. Passerini, *J. Chem. Soc. Perkin Trans. 2* (1977) 309.
- [35] N.C. Marziano, A. Tomasin and P. Traverso, *J. Chem. Soc. Perkin Trans. 2* (1981) 1070.
- [36] N.C. Marziano, A. Tomasin and C. Tortato, *Org. React. (Tartu)* 30 (1996) 29.
- [37] N.C. Marziano, A. Tomasin and C. Tortato, *Org. React. (Tartu)* 30 (1996) 39.
- [38] J.M. Riego, Z. Sedin, J. Zaldivar, N.C. Marziano and C. Tortato, *Tetrahedron Lett.* 37 (1996) 513.
- [39] M. Attinà, F. Cacace and M. Yanez, *J. Am. Chem. Soc.* 109 (1987) 5092.
- [40] N.C. Marziano, C. Tortato, A.A. Sheikh-Osman, J. Riego and J.M. Zaldivar, *Org. React. (Tartu)* 30 (1996) 49.
- [41] N.C. Marziano, C. Tortato, A.A. Sheikh-Osman, J. Riego and J.M. Zaldivar, *Org. React. (Tartu)* 31 (1997) 87.
- [42] N.C. Marziano, A.A. Sheikh-Osman, C. Tortato, L. Ronchin, unpublished results.
- [43] G.A. Olah, R. Malhotra and S.C. Narang, *J. Org. Chem.* 43 (1978) 4628.
- [44] L. Berteau, H.W. Kouwenhoven and R. Prins, *Appl. Catal. A* 129 (1995) 229.
- [45] K. Smith, A. Musson and G.A. DeBoos, *J. Chem. Soc. Chem. Commun.* (1996) 469.