# Clay catalysed nitrodecarboxylation of aromatic acids

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Nitration of *p*-anisic acid in clay microenvironment yields 2,4-dinitroanisole in about 40–60% yield, in addition to the conventional nitration product, namely 3-nitro-4-methoxybenzoic acid. While clay directed nitration of *p*-methoxyacetophenone gives only 3-nitro-4-methoxyacetophenone, with *m*-nitrobenzoic acid, nitrodecarboxylation yielding *m*-dinitrobenzene is the only reaction course. The observed greater ipso-nitration facilitated by a nitro group may be attributed to the greater ease with which the Wheland intermediate may decompose via a cyclic six-membered transition state.

**Keywords**: Montmorillonite clay; catalysis; nitrodecarboxylation

## 1. Introduction

There is considerable interest in clays and clay-supported reagents in recent years [1–4]. Acidic cation-exchanged montmorillonites are efficient solid acid catalysts in a number of proton assisted reactions [5]. Clay-supported reagents enjoy advantages as restricted diffusion of reaction partners, microenvironments of differing polarity with acidic (or basic) sites, activation or stabilisation of substrates, promotion of selective modes of reaction, ease of work-up etc.

In a recent report on nitration of *p*-anisaldehyde in the presence of montmorillonite clays [6], along with the conventional nitration product, i.e., 3-nitro-4-methoxybenzaldehyde, a small amount of the ipso-nitration product (4-nitroanisole) is also formed. Its proportion increases (10–20%) as the Brønsted acidity of the montmorillonite clay is enhanced by the Lewis acidic interstitial cations. With kaolinite clays, also having strongly acidic surfaces, ipso-nitration is still more pronounced (27%). This prompted us to investigate the nitration of *p*-anisic acid, *p*-methoxyacetophenone and *m*-nitrobenzoic acid in the presence of natural as well as cation-exchanged montmorillonite clays with a view to study the role of clays in

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the nitration and also to probe their catalytic efficiency and mechanism. The results are discussed in the following pages.

## 2. Experimental

### 2.1. REAGENTS

*p*-anisic acid (Sisco-Chem, LR) and *m*-nitrobenzoic acid (Sisco-Chem, LR) were recrystallised repeatedly from ethanol and were used for the reaction. *p*-methoxyacetophenone was prepared from the reaction of *p*-hydroxyacetophenone with dimethyl sulphate and sodium hydroxide.

### 2.2. PREPARATION OF CATALYSTS

Cation-exchanged montmorillonite clay was prepared [5,7] by stirring 1 g of natural clay with 25 ml of 1 M solution of the appropriate salt (nitrate or chloride) for 3 days. It was then filtered, washed repeatedly with distilled water and dried at 60°C.

### 2.3. NITRATION PROCEDURE

0.2 g of the starting material was powdered well and mixed intimately with an equal or excess amount of either natural or exchanged clays. The mixture was taken in a round-bottomed flask and 1–2 ml of fuming nitric acid was added dropwise. Nitration was carried out [8] at low as well as high temperatures depending on the substrate. For nitration at elevated temperatures the round-bottomed flask was fitted with a water condenser and warmed in a water or oil bath. The reaction mixture was then poured into water, filtered and extracted with ether. After evaporation of the ether layer, the residue was analysed by h.p.l.c.

### 2.4. ANALYSIS OF THE REACTION MIXTURE

The percentage conversion and the relative amounts of the different products in the final mixture were obtained by analysing in a Shimadzu LC-6A modular h.p.l.c. system (reverse phase column (ODS), UV-detector at 254 nm) using methanol as the mobile phase and in each case the retention time for the starting material was taken as the internal reference. Nitration products were identified by coinjection with authentic samples, prepared by known methods. NMR spectra for the starting materials and the different nitration products are recorded in a Perkin-Elmer 90 MHz NMR instrument. IR spectra were taken in a Perkin-Elmer (model 577) instrument.

## 3. Results and discussion

### 3.1. NITRATION OF *p*-ANISIC ACID

Results of nitration of *p*-anisic acid (I) using fuming nitric acid carried out in clay microenvironment under various conditions are summarised in table 1. It is amply clear that the nitration proceeds very smoothly and efficiently under the reaction conditions. In a blank experiment performed in the absence of clay, the carboxyl group is not displaced and 3-nitro-4-methoxybenzoic acid (II) is the only product obtained. When carried out in the presence of clays, in addition to product (II), 2,4-dinitroanisole (III) is also formed (scheme 1) in significant yields (the yield of III is about 40–60% under various conditions as listed in table 1). It is interesting to note that clay-catalysed nitrodecarboxylation takes place more readily in *p*-anisic acid compared to *p*-anisaldehyde [6] wherein even under the most favourable circumstances, ipso-nitration is only about 27%. The observed greater ipso-nitration for I may be attributed to the greater ease with which the Wheland intermediate (leading to III) may decompose via a cyclic six-membered transition state (scheme 2).

The other significant features are (a) a longer refluxion time favours the conventional nitration product (II), (b) increasing the amount of clay improves the yield

Table 1
Product distribution [a] in the nitration of *p*-anisic acid (I)

| Conditions | Reaction temp. (°C) | Reaction time (min) | Conversion (%) | Yield (%) | |
|---|---|---|---|---|---|
| | | | | II | III |
| fuming nitric acid | b | 30 | 100 | 100 | – |
| K10–mont. (1 : 1) [c] | b | 30 | 100 | 54 | 46 |
| K10–mont. (1 : 1) | b | 60 | 100 | 64 | 36 |
| K10–mont. (1 : 1) | b | 120 | 100 | 69 | 31 |
| K10–mont. (1 : 1) | b | 480 | 100 | 73 | 27 |
| K10–mont. (1 : 2) | 0–5 | 30 | 100 | 43 | 57 |
| K10–mont. (1 : 2) [d] | – | – | 100 | 51 | 49 |
| K10–mont. (1 : 2) [e] | – | – | 100 | 54 | 46 |
| K10–mont. (1 : 2) | 10 | 30 | 100 | 44 | 56 |
| K10–mont.–$H^+$ (1 : 2) | b | 30 | 100 | 58 | 42 |
| K10–mont.–$Al^{3+}$ (1 : 2) | b | 30 | 100 | 58 | 42 |
| K10–mont.–$Fe^{3+}$ (1 : 2) | b | 30 | 100 | 57 | 43 |

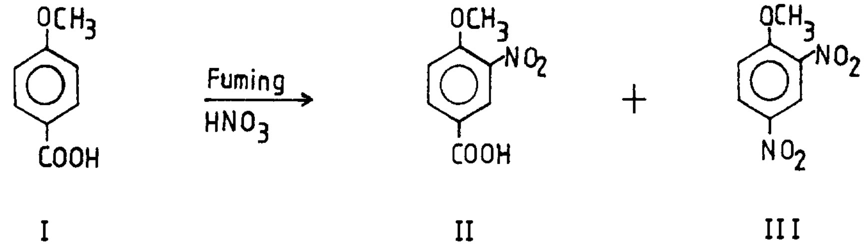
[a] Analysed by h.p.l.c; error limit ±3%.

[b] Refluxed in a water bath.

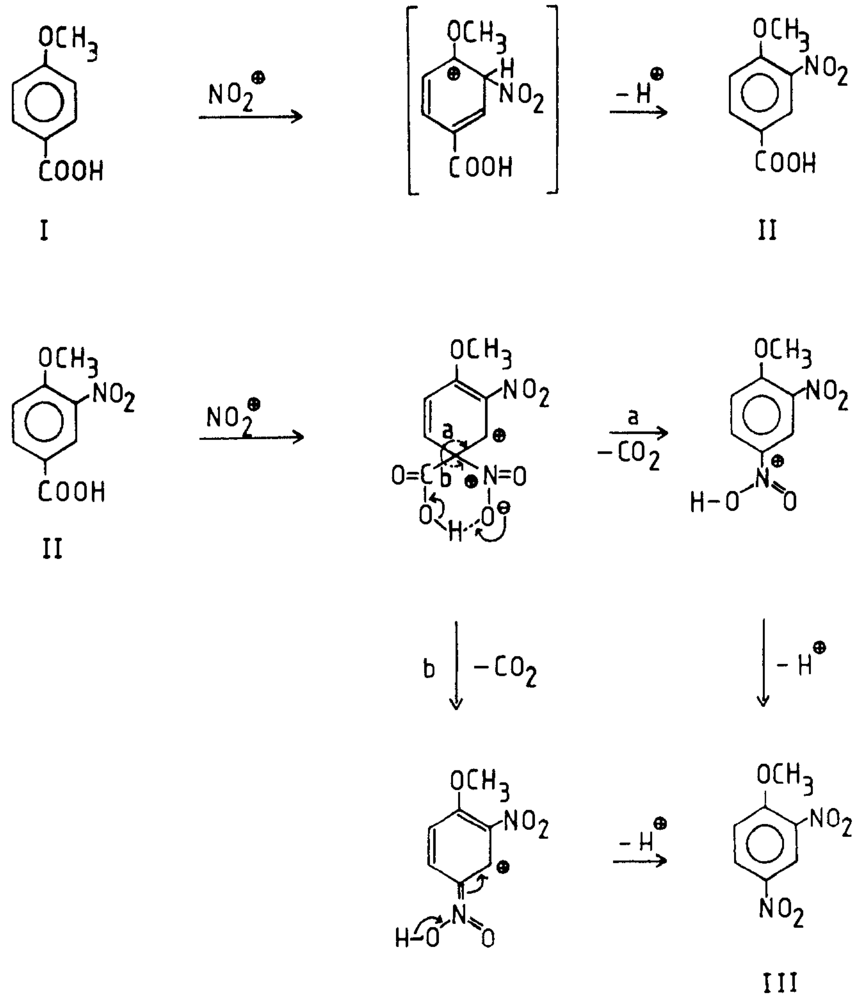
[c] The ratios in parentheses refer to that of substrate : clay.

[d] Fuming nitric acid was added dropwise to the reaction mixture placed in a freezing mixture. The mixture was then kept aside at room temperature for 30 min.

[e] The clay substrate mixture was stirred magnetically in water, filtered, dried at 50°C and nitric acid was added dropwise at room temperature. The mixture was kept aside for 30 min.



Scheme 1.



Scheme 2.

of III, (c) even with natural clay, the yields are good and (d) the product distribution is unaffected in the presence of exchanged clays such as K10–$H^+$, K10–$Al^{3+}$, K10–$Fe^{3+}$ etc. It is more likely that the presence of nitric acid may have resulted in considerable disruption of the interlamellar structure, including the loss of exchanged cations. Hence, all the ion-exchanged as well as natural clays have yielded essentially the same results.

It was already reported by Barbier [9] and Alfthan [10] that in the nitration of benzene derivatives in which a nitro group displaces an alkyl (or acyl) group, the group displaced was always meta to the first entering nitro-group. The catalytic role of clays in nitrodecarboxylation may be attributed to the very strongly acidic environment provided by them to activate or stabilise the already mononitrated substrate to undergo further nitration. The acidic sites of clay further bind the substrate in enzyme-like pockets, thereby promoting a selective mode of attack.

It is quite likely that even in the nitration of *p*-anisaldehyde [6], ipso-nitration may take place by initial oxidation of the aldehydic group followed by its subsequent decarboxylation. It is significant to note that at elevated temperatures [11], nitric acid tends to act as an oxidising agent rather than as a nitrating agent.

### 3.2. NITRATION OF *p*-METHOXYACETOPHENONE

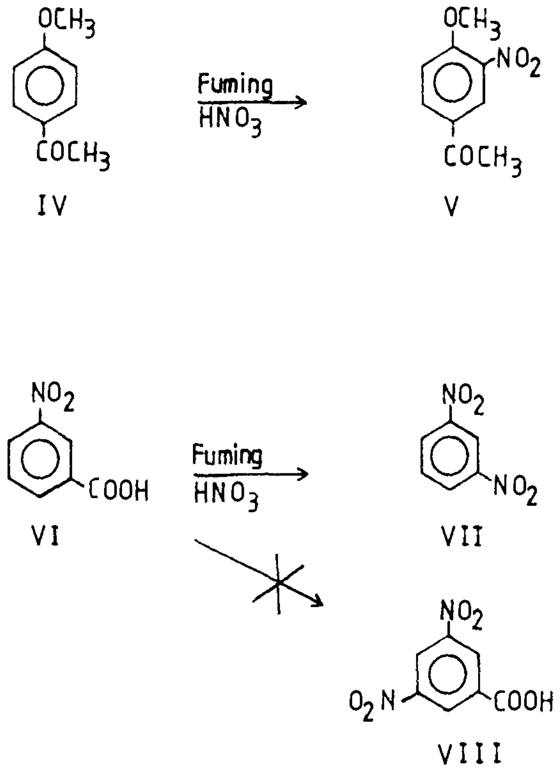
In contrast to the nitration of *p*-anisic acid, clay-directed nitration of *p*-methoxyacetophenone (IV) when carried out under analogous conditions yields only the conventional nitration product, i.e. 3-nitro-4-methoxyacetophenone (V) (scheme 3). This is in accordance with the reluctance of the acetyl group to get displaced upon attack by an electrophile.

### 3.3. NITRATION OF *m*-NITROBENZOIC ACID

The observed ease of displacement of the carboxyl group in the nitration of *p*-anisic acid (I) prompted us to study the nitration of *m*-nitrobenzoic acid in clay microenvironment and the results are summarised in table 2.

The observed significant features of clay-directed reaction are (a) nitration takes place at a much slower rate when compared with *p*-anisic acid (I) and *p*-methoxyacetophenone (IV) in accordance with the deactivation of the aryl ring by both nitro and carboxyl groups, (b) the conventional nitration product namely, 3,5-dinitrobenzoic acid (VIII) is conspicuously absent though this is the exclusive product in the absence of clays, (c) ipso-nitration resulting in the removal of the carboxyl group is the only reaction course and *m*-dinitrobenzene (VII) is the exclusive product, (d) presence of cation-exchanged ($H^+$, $Fe^{3+}$, $Co^{2+}$, $Cu^{2+}$, $Cr^{3+}$) montmorillonites and also excess clay has no significant effect on the reaction. However, $Al^{3+}$-exchanged montmorillonite exhibits a very significant effect on the reaction improving the overall yield to 44%.

The results of nitration of *m*-nitrobenzoic acid indicate clearly that nitrodecar-



Scheme 3.

Table 2
Product distribution[a] in the nitration of *m*-nitrobenzoic acid (VI)

| Conditions[b] | Reaction time (min) | Conversion (%) | Yield (%) | |
|---|---|---|---|---|
| | | | VII | VIII |
| fuming nitric acid | 180 | 20 | – | 100 |
| K10–mont. (1 : 1) | 240 | 5 | 5 | – |
| K10–mont. (1 : 1) | 480 | 8 | 8 | – |
| K10–mont.–$H^+$ (1 : 1) | 240 | 5 | 5 | – |
| K10–mont. (1 : 1) | 960 | 14 | 13 | 1 |
| K10–mont. (1 : 2) | 960 | nil | – | – |
| K10–mont.–$Al^{3+}$ (1 : 2) | 960 | 44 | 44 | – |
| K10–mont.–$Co^{2+}$ (1 : 2) | 960 | 8 | 8 | – |
| K10–mont.–$Fe^{3+}$ (1 : 2) | 960 | 8 | 8 | – |
| K10–mont.–$Cr^{3+}$ (1 : 2) | 960 | 10 | 10 | – |
| K10–mont.–$Cu^{2+}$ (1 : 2) | 960 | 6 | 6 | – |

[a] Analysed by h.p.l.c; error limit ±3%.

[b] The reaction mixture was refluxed in an oil bath and the temperature was maintained at 130–140°C.

boxylation is favoured at elevated temperatures [11] and a nitro group already present will direct the reaction more towards nitrodecarboxylation rather than simple nitration. This may be attributed to the facile decomposition of the Wheland intermediate via a cyclic six-membered transition state (scheme 2).

## 4. Conclusions

This paper has highlighted the efficiency and selectivity of natural as well as cation-exchanged montmorillonite clays in promoting nitrodecarboxylation in the nitration of aromatic carboxylic acids. In fact, with a suitable substrate as *m*-nitrobenzoic acid, nitrodecarboxylation is the exclusive reaction path. The active role of the first-entering nitro group, facile decomposition of the Wheland intermediate and the catalytic efficiency of clays are also discussed thus providing an interesting insight into the applications of clay chemistry.

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