# CATALYTIC ACTIVITY OF THE BLEACHING CLAY ON CONDENSATION OF METHYL-N-PHENYLCARBAMATE WITH METHYLENATION AGENTS

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**Abstract:** Among the many kinds of clay minerals, montmorillonite has been most often used in organic chemical applications. The use of acid activated montmorillonite clays as catalyst in organic synthesis was briefly reviewed. The use of the commercial bleaching clay as a catalyst was investigated. Dimethyl 4,4'-diphenylmethane dicarbamate and polymethylene polyphenyl carbamate homologues were prepared by the bleaching clay catalyzed condensation of an methyl N-phenylcarbamate with a methylenation agent, such as formaldehyde or trioxane. The influence of the catalyst used, the ratio of the catalyst to methyl N-phenylcarbamate, the molar ratio of methyl-N-phenylcarbamate to the methylenation agent, temperature and reaction time on yields of dimethyl 4,4'-diphenylmethane dicarbamate was examined. The condensation products were analyzed by high-performance liquid chromatography on reversed phases ( RP-HPLC ).The bleaching clay can be used as an efficient catalyst of condensation of methyl-N-phenylcarbamate with formaldehyde.

**Key words:** bleaching clay, H-montmorillonite, dimethyl 4,4'- diphenylmethane dicarbamate, RP-HPLC.

## Introduction

Clay minerals have many desirable properties including a high sorption capacity, shape specificity, localized acidity and restricted movement of water molecules. Clay minerals increasingly attract attention as sorbents and catalysts and are considered for selective removal of organic and inorganic pollutants. Among the many kinds of clays, montmorillonite (MMT) has often been used in organic chemical applications, both environmental and technological. MMT is also known as a naturally occurring inorganic catalyst. Its catalytic role has been recognised in chemical transformations in soils or sediments (Strachan et al. 1988). The knowledge of their interaction with pesticides and fertilizers is also important in forecasting the attenuation and fate of toxic substances in a natural environment. Catalysis by MMT has attracted the most interest because of the possible application in environmental hazardous waste disposal and in organic synthesis. The diversity of clay behavior and applications is apparent in a large number of recent papers. Excellent reviews have been published by Barrer (1989), Laszlo (1987), Ortego et al. (1991), Thomas & Theocharis (1992) and Soma & Soma (1987). The diversity of MMT properties is derived primarily from its structure. MMT is a three-layer clay. The ideal formula (1/2 unit cell) of MMT is:

$$(Al_{2-x}Mg_x) ( Si_{4-y}Al_y) O_{10}(OH)_2 M^+_{x+y}. n H_2O \quad (1)$$
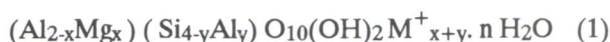
where M is an interlayer cation, x and y are the octahedral and tetrahedral substitutions, respectively, and x>y (Ortego et al. 1991). MMT clays are commonly the main constituents of bentonite clays (Číčel et al. 1992a; Kraus et al. 1989; Fajnor et al. 1992; Jesenák & Šucha 1992). These clays have a 2 : 1 layer type structure, where an octahedral aluminate sheet is sandwiched between two tetrahedral silicate sheets.

The $Na^+$ forms of MMT clays show only a low catalytic activity towards organic molecules, but, various cation-exchanged MMT clays are effective for a wide range of organic reactions. Those promoting strong acidic strength of clays can be expressed by the Hammett acidity function, $H_o$ :

$$H_o = pK_a + \log [B]/[BH]^+ = pK_a + \log [B]/[AB] \quad (2)$$

where [B] and [BH⁺] are the concentrations of the base and its conjugated acid and AB is the concentration of the addition product formed adsorption onto a Lewis site (Benesi 1957).

The synthesis of commercially valuable products with acid activated and chemically modified clays as catalysts represents a new area for research. The reactions performed with MMT often display an increase in selectivity when compared to the analogous homogeneous reaction. This is probably due to special requirements for the bonding of reactive species around the interlamelar cation.

**Table 1:** Condensation products of methyl N-phenylcarbamate with methylenation agent as determined by RP-HPLC.

| Run | Catalyst | Molar ratio | | Solvent | T [°C] | Time [min] | Yield [wt.%] | |
|-----|----------|-------------|-----|---------|--------|------------|------|-------|
|     |          | Cat/MPC | MPC/HCOH |     |        |            | MDDC | PMPPC |
| 1[a] | bleaching clay | 28 wt.% | 8.8 | cyclohexane | 81 | 240 | - | - |
|     |          |         | -   |         | 110 | 600 | 67.5 | 6 |
| 2[a] | bleaching clay | 28 wt.% | 8.8 | cyclohexane | 81 | 240 | - | - |
|     |          |         | -   |         | 110 | 1020 | 74.6 | 1 |
| 3[a] | bleaching clay | 28 wt.% | 8.8[b] | cyclohexane | 81 | 240 | - | - |
|     |          |         | -   |         | 110 | 600 | 56.4 | 4 |
| 4[a] | nonactivated bentonite | 28 wt.% | 8.8 | cyclohexane | 81 | 240 | - | - |
|     |          |         | -   |         | 110 | 600 | 0.12 | - |

[a] two-step condensation process; [b] methylenation agent is trioxane

Several ion-exchanged Wyoming bentonites were succesfully examined as catalysts in the reaction of ethylene and acetic acid to yield ethyl acetate (Gregory et al. 1983):

$$CH_2=CH_2 + CH_3COOH \rightarrow CH_3COOCH_2CH_3 \quad (3)$$

It was determined that for this reaction, the order of activity ion-exchanged bentonite is: $H^+ >> Al^{3+} > Cr^{3+} > Fe^{3+} > Cu^{2+} > Na^+$.

Choudary et al. (1991) developed a new system comprising H-montmorillonite and $KMnO_4$ for the oxidation of alkenes to dicarboxylic acids. An acid activated mixture of kaolinite-palygorskite-illite-MMT was succesfully tested as a catalyst in the thermal polymerization of styrene (Njopwouo et al. 1987). Acid treatment of montmorillonite was reported recently as a support for $ZnCl_2$ Friedel-Crafts alkylation catalysts (Rhodes et al. 1991) and as a catalyst for the dehydration and esterification of 1-hexanol (Breen 1991). Acid activated MMT clays (H-montmorillonites) can catalyse the conversion of toluene to nitrotoluene, using $PhCOONO_2$ as the nitrating agent in a $CCl_4$ solution (Cornélis et al. 1988). H-montmorillonites as a source of protons can be used in dimerization of oleic acid (Číčel et al. 1992) and also in industrial petroleum cracking (Pinnavaia 1983, Youssef et al. 1989). Acid treatment of bentonites is widely used in industry for bleaching clay and catalyst production.

The aim of this paper was to investigate the use of the bleaching clay as a heterogeneous catalyst for dimethyl 4,4'- diphenylmethane dicarbamate (4,4'-MDDC) and polymethylene polyphenyl carbamates (PMPPC) preparation as condensation products of methyl-N-phenylcarbamate (MPC) with methylenation agents. These compounds are important precursors for preparation of diphenylmethane diisocyanates and the mixtures of diisocyanates and polyisocyanates, which are valuable intermediates in the production of polyurethane materials (Jakuš 1991a).

## Experimental

### Materials

The bleaching clay as commercial bentonite from locality Stará Kremnička-Jelšový Potok (Kremnické vrchy Mts., Central Slovakia) activated by HCl (Istrochem, Bratislava) was used as a catalyst of condensation of MPC with formaldehyde (37 wt. % aqueous solution stabilized with 1 wt. % methanol, Chemko, Strážske) or trioxane (Fluka). MPC was prepared by reductive carbonylation of nitrobenzene in the presence of methanol (Jakuš & Bojsová 1992).

### Methods

A mixture of MPC, bleaching clay and an inert solvent were heated with stirring to the required temperature, formaldehyde or trioxane was introduced under concurrent removal of water by azeotropic distillation together with a part of the inert solvent. The inert solvent was then distilled and reaction mixture was stirred at a higher temperature. After finishing the reaction, acetone dissolving all reaction components was added, the mixture was filtered and filtrate was worked up (Jakuš 1991b). MPC and condensation products (4,4'-MDDC and PMPPC) were then analyzed by high performance liquid chromatography on reversed phases (RP-HPLC). The above mentioned compounds were separated from the remaining components of the mixture by RP-HPLC using the isocratic elution mode. A direct method was applied for calibration.

*Analysis conditions:* high-resolution liquid chromatograph (Laboratorní přístroje, Praha), column 150 x 3.3 mm i.d. packed with Separon CGC, 5μm grain size.

*Mobile phase:* methanol/water 6:4 (v/v), flow rate 0.3 ml.min$^{-1}$, detector UV$_{254}$, injected amount 5 μl of methanolic solution, chart drive 0.15 cm.min$^{-1}$.

The content of constituents in samples (in wt. %) was calculated according to the following equation

$$c = (A_s R_F 100)/n \quad (4)$$

**Table 2:** Effect of the ratio catalyst/MPC on MDDC yield.

| Run | Catalyst | Molar ratio | | T [°C] | Time [min] | Yield [wt.%] |
| | | Cat/MPC | MPC/HCOH | | | MDDC |
|---|---|---|---|---|---|---|
| 1 | bleaching clay | 9 wt.% | 8.8 | 81 | 680 | 14.1 |
| 2 | bleaching clay | 28 wt.% | 8.8 | 81 | 680 | 49.1 |
| 3 | bleaching clay | 54 wt.% | 8.8 | 81 | 680 | 55.3 |

**Table 3:** Effect of the molar ratio MPC/HCOH on MDDC yield.

| Run | Catalyst | Molar ratio | | T [°C] | Time [min] | Yield [wt.%] |
| | | Cat/MPC | MPC/HCOH | | | MDDC |
|---|---|---|---|---|---|---|
| 1 | bleaching clay | 28 wt.% | 2.2 | 81 | 680 | 36 |
| 2 | bleaching clay | 28 wt.% | 4.6 | 81 | 680 | 45 |
| 3 | bleaching clay | 54 wt.% | 11.3 | 81 | 680 | 51 |

**Table 4:** Effect of the temperature on MDDC yield.

| Run | Catalyst | Molar ratio | | T [°C] | Time [min] | Yield [wt.%] |
| | | Cat/MPC | MPC/HCOH | | | MDDC |
|---|---|---|---|---|---|---|
| 1 | bleaching clay | 28 wt.% | 8.8 | 70 | 680 | 32.1 |
| 2 | bleaching clay | 28 wt.% | 8.8 | 96 | 680 | 52.2 |
| 3 | bleaching clay | 28 wt.% | 8.8 | 110 | 680 | 54.7 |

**Table 5:** Effect of the time on MDDC yield.

| Run | Catalyst | Molar ratio | | T [°C] | Time [min] | Yield [wt.%] |
| | | Cat/MPC | MPC/HCOH | | | MDDC |
|---|---|---|---|---|---|---|
| 1 | bleaching clay | 28 wt.% | 8.8 | 81 | 240 | 41.0 |
| 2 | bleaching clay | 28 wt.% | 8.8 | 81 | 520 | 43.8 |
| 3 | bleaching clay | 54 wt.% | 8.8 | 81 | 850 | 53.4 |

where c is the substance content, $A_s$ the peak area of the compound determined in the sample, $R_F$ the response factor of the given compound, n the amount of samples.
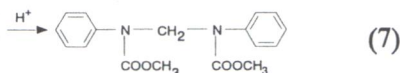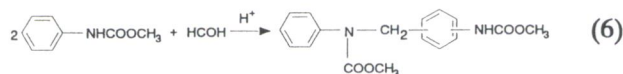
## Results and discussion

Studies of the condensation of MPC with methylenation agents (see Tab. 1) have shown that 4,4'-MDDC can be prepared in high yields by reacting MPC with formaldehyde in the presence of an acid catalyst:
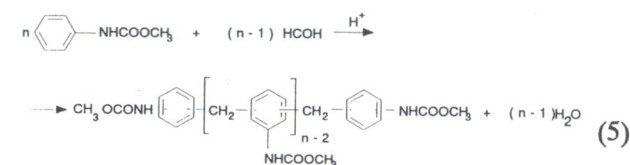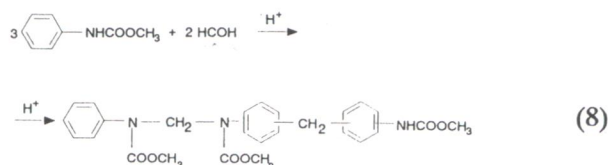


$$ \text{if } n = 2 \longrightarrow \text{MDDC}, \quad n = 3 \longrightarrow \text{MTTC}, \quad n > 3 \longrightarrow \text{PMPPC} $$

Condensation of methyl N-phenylcarbamate with formaldehyde can give further isomers possessing a tertiary nitrogen and having the carbamate nitrogen bonded through the methylene bridge (N-benzyl derivatives):
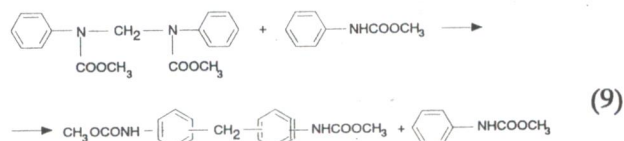


and/or



As found (Jakuš 1991b), these N-benzyl derivatives can undergo an intermolecular transfer reaction in the presence of alkyl N-phenylcarbamate and at temperatures higher than 81 °C to give the corresponding diphenylmethane dicarbamates and polymethylene polyphenylcarbamates:



Therefore the highest MDDC yield (67.5 and 74.6 wt. %, resp.) was obtained at an excess of MPC with bleaching clay (bentonite activated by HCl 32 wt. %) in a two-step condensation process. Application of nonactivated bentonite led to 0.12 wt. % yield of MDDC only. In Tab. 2 is presented the positive influence of the amount of the catalyst used. Increasing of the molar ratio MPC/HCOH leads to an increased MDDC yield (see Tab. 3). The temperature influence in the case of one-step condensation is presented in Tab. 4. Longer reaction times lead to higher MDDC yields as it can be seen from Tab. 5.

## Conclusions

The results reported in the present article have shown that the nonactivated bentonite from locality Kremnička-Jelšový Potok was a totally ineffective catalyst of condensation of methyl N-phenylcarbamate with methylenation agents. Acid treatment of bentonite (bleaching clay) has been shown to increase its effectiveness significantly as a catalyst of condensation of methyl-N-phenylcarbamate with formaldehyde. The catalytic activity can probably be improved by increasing of acidity of the bleaching clay, which depends on the level of structure decomposition of the bentonite.

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