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Electrophilic chlorination of arenes with trichloroisocyanuric acid over acid zeolites

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ABSTRACT

Trichloroisocyanuric acid (TCCA) reacts with arenes and its reactivity is highly affected by the acid strength of the reaction medium. Deactivated arenes are efficiently chlorinated by TCCA in solid acids. Our experimental results, along with DFT calculations show that chlorination using solid acid catalysis is feasible, thus leading to possible replacement of strong liquid acids used to promote this superelectrophilic reaction. We have tested several solid acids, showing the synergic need for acid strength and pore size for promoting the reaction.

1. Introduction

Electrophilic reagents that have greatly enhanced reactivities in the presence of superacids are said to form protonated or protosolvated species, named as superelectrophiles by Olah [1]. The concept of using charge–charge repulsion into the reagents in order to decrease the activation barrier was explored for a series of reactions, especially by Klumpp et al. [2]. We have been using this concept for halogenating organic substrates using trihaloisocyanuric acids (TXCA, Fig. 1) [3–5].

Trichloroisocyanuric acid (TCCA) is a safe commercially available reagent [6], whilst tribromo- and triiodoisocyanuric acids (TBCA and TICA, respectively) can be prepared from readily available commercial sources [7,8]. These reagents can perform the electrophilic halogenation of diverse substrates, such as alkenes [9,10] and carbonyl compounds [11]. The trihaloisocyanuric acids containing different halogen atoms are also powerful regioselective halogenating agents [12,13].

The trihaloisocyanuric acid can also be efficiently used to introduce halogen atoms into electron rich arenes [14–16]. On the other hand, the reaction with deactivated arenes is only possible under strong acid conditions [17], the reactivity being highly influenced by the acidity of the reaction medium [3]. As an example, nitrobenzene is fully brominated to the pentabromonitrobenzene by TBCA in 2 min at room temperature by using 65% oleum as solvent [4]. Other impressive results are the electrophilic chlorination [3], bromination [4], and iodination [5] of *m*-dinitrobenzene respectively by TCCA, TBCA and TICA in 98% H_2SO_4, which afforded the corresponding halogenated products in good yields.

The use of strong acids is however a drawback due to its high corrosive nature and environmental problems. In order to solve this problem and render the halogenating process safer, we have considered the use of solid acids as an alternative to liquid acids. Recently, zeolites and other solid acids have been shown to be attractive catalysts because in addition to maintaining the electrophilic character of the medium sharp, do not generate waste and are easily removed at the end of the reaction by simple filtration [18,19]. Despite being much less acidic than 98% H_2SO_4, they possess a number of other properties based on their structure that can influence the progress of reactions [20]. One of them is the catalytic activity of acid catalysed processes, due primarily to the presence of Brønsted acid sites [21].

Acid zeolite catalysis has been used in electrophilic aromatic substitution reactions [22,23]. Various reagents have been used in zeolite-catalysed chlorination of arenes [23]. However, they are not safe (Cl_2, *t*-butyl hypochlorite, sulfuryl chloride, to name a few) or

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the reactions suffer from lack of chemoselectivity. On the other hand, limited studies have been reported involving the use of *N*-halo compounds in halogenation reactions catalysed by solid acids [24].

Based on the above considerations, we wish to report here our results on the reaction of aromatic compounds with the system TCCA/solid acids.

2. Experimental

2.1. Materials and methods

Trichloroisocyanuric acid (Aldrich, 98%), toluene (Carlo Erba, 99%), chlorobenzene (SDS, 99%), nitrobenzene (Merck, 99%) and solvents were used as received. Different commercial zeolites were tested H-USY (Zeolyst, CBV500), H-BEA (Zeolyst), H-EMT (IS2M, UHA, Mulhouse), H-MOR (Zeolyst), H-ZSM-5 (Zeolyst CBV30/24) and H-SAPO-5 (Louvain University, Belgium). Prior to use, these zeolites were activated at 550 °C in static air for 4 h. Non-zeolitic catalysts were used as received: Nafion SAC-13 (Aldrich, 20% nafion in MCM-41, SSA = 418 m^2/g), SO_4^{2-}/ZrO_2 (SSA = 97 m^2/g) [32] and $H_3PW_{12}O_{40}$ (Aldrich, SSA = 5 m^2/g).

The quantification of the Brønsted acid sites present in different solid acids was performed according to our home-developed H/D exchange isotope technique [25–28]. This method is based on the deuteration of the catalyst by sweeping D_2O with nitrogen (3 mol%) for 1 h at 200 °C. After purging the excess of D_2O for 2 h, the D-solid acid catalyst was contacted with water vapor to perform the back exchange of the Brønsted acid sites. Meanwhile, partially exchanged water (H_xOD_y) was collected in a cold trap. A double-excess of trifluoroacetic anhydride was then added and this acid solution was then analyzed by 400 MHz ^1H and ^2H NMR ($CDCl_3/CHCl_3$ mixture used as internal standard). The acid site density was then calculated based on the H/D ratio determined by NMR and the weight of H_xOD_y condensed as already reported elsewhere [25–28].

Analyses of the reactions were carried out using a GC chromatograph with FID using a 30 m (length), 0.25 mm (ID), and 25 μm (phase thickness) RTX-5 capillary column and H_2 (flow rate 50 cm/s) as carrier gas (split: 1:10). The chlorinated products were confirmed by co-injections with the authentic samples and by GC–MS analyses performed on a Shimadzu GCMS-QP2010S gas chromatograph with electron impact (70 eV) by using a 30 m DB-5 silica capillary column.

2.2. DFT calculations

All calculations were carried out using the M06-2X functional and 6-31++G**(C,N,O,H) and ECP(Si,Al,Cl) basis set (see ECP below). Minima on the potential energy surface were characterised by absence of the harmonic frequencies of the respective optimized structures, while the transition state presents a single imaginary frequency after vibrational analysis. Further IRC analysis confirmed that the transition state connects HT5.TCCA.HT5 to σ-complex 1. All energy differences correspond to enthalpy differences at 298.15 K and 1 atm. The calculations include solvation using the IEFPCM(H_2O) [29]. All calculations were carried out using the Gaussian 09 package [30].

2.3. Chlorination of arenes with TCCA/solid acid

2.3.1. General procedure for chlorination of toluene

TCCA (0.34 mmol) was added at room temperature in small portions to a well-stirred suspension of toluene (1 mmol) and the solid acid (0.3 mmol H^+) in CH_2Cl_2 (5 mL). After completion of the reaction (determined by GC), the reaction mixture was filtered and the solid was washed with CH_2Cl_2 (5 mL) in small portions. The resulting solution was treated with 10% aqueous $Na_2S_2O_3$ (5 mL), washed with water (5 mL) and then dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was analyzed by GC.

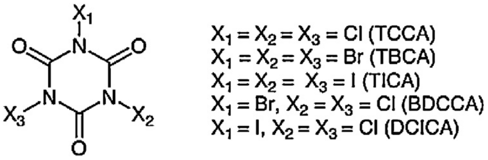

Fig. 1. Some trihaloisocyanuric acids.

2.3.2. General procedure for chlorination of chlorobenzene

TCCA (0.6 mmol) was added at room temperature to a well-stirred suspension of chlorobenzene (1.8 mmol) and the solid acid (0.54 mmol H^+) in the appropriated solvent (10 mL, see Table 3). After 24 h (reflux or room temperature), the reaction mixture was cooled, filtered and the solid washed with 1,2-dichloroethane (5 mL) in small portions. The resulting solution was treated with 10% aq. $Na_2S_2O_3$ (8 mL), washed with water (8 mL) and then dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was analyzed by GC.

2.3.3. Chlorination of nitrobenzene with TCCA/H-USY zeolite under flow conditions

The chlorination reaction of nitrobenzene was performed in a glass flow system with a cylindrical reactor as reported elsewhere [29]. The gas flow was regulated by means of Brooks 5850E mass flow controllers and the dry nitrogen flow was set to 100 mL/min for each experiments. The reaction was carried out by diluting the catalytic bed (TCCA and H-USY) in an amorphous silica (Grace, USA) matrix to insure the same height for all catalyst beds. H-USY zeolite (0.44 mmol H^+), TCCA (0.15 mmol) and silica matrix (17 mmol, 1 g) were blended closely by grinding. The mixture was then transferred to the cylindrical reactor and the reactor was fixed to the set-up. The catalytic bed was first dried under dry N_2 flow at 150 °C for 30 min to desorb the water present in the void volume of the zeolite. Then, nitrobenzene was supplied in its gaseous state by sweeping a dry N_2 flow through a stripping U-shaped reactor containing liquid nitrobenzene at room temperature. Hence, this dry nitrogen flow saturated with nitrobenzene's vapor pressure was allowed to pass through the catalytic bed during 5 h. The products were trapped at −196 °C and recovered downstream to the reactor with toluene (4 mL). After evaporation of the solvent, the residue was analysed by GC.

3. Results and discussion

In our study, we tested the reaction of trichloroisocyanuric acid with model arenes with different nucleophilic degrees (in decreasing order of reactivity with an electrophile): toluene, chlorobenzene, and nitrobenzene. Table 1 presents the several solid acids of different nature and characteristics (such as microporous zeolites and mesoporous acids) chosen as catalysts for the reaction. The reactions were typically performed in a round bottom flask under magnetic stirring, using 1 mmol of the aromatic substrate, TCCA (0.34 mol equiv.), a given amount (corresponding to 0.3 mol equiv. of H^+) of the acid solid and CH_2Cl_2 or 1,2-dichloroethane as solvents.

The results of the reaction of toluene with TCCA using several solid acids as catalysts are shown in Table 2. One can observe that