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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.

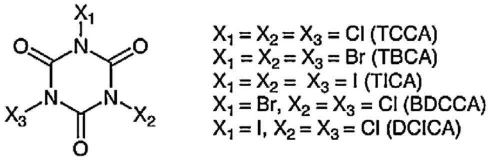


Fig. 1. Some trihaloisocyanuric acids.

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

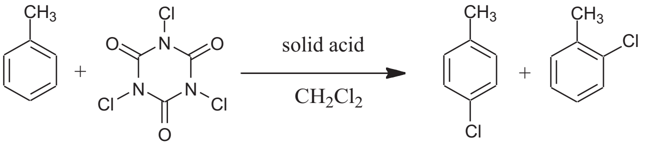
In our study, we tested the reaction of trichloroisocyanuric acid with model arenes with different nucleophilic degrees (in decreasing order of reactivity with an electrophile): toluene, chlorobenzene, and nitrobenzene. Table 1 presents the several solid acids of different nature and characteristics (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

Table 1
Solid acids studied in the reaction of arenes with TCCA.

Solid acid	Characteristic	Pore size (Å) [31]	mmol H$^+$/g	Si/Al	Crystal size (μm)
H-USY	Microporous zeolite	7.4	3.9	2.9	0.5–0.7
H-BEA	Microporous zeolite	5.6	1.1	13.6	0.4
H-EMT	Microporous zeolite	7.4	2.4	6.5	2
H-MOR	Microporous zeolite	7.0 × 6.5	1.5	10	1–1.5
H-ZSM-5	Microporous zeolite	5.5	1.0	15	0.8–1
NAFION/MCM-41	Polymer on MCM-41	20	1.0	–	–
H-SAPO-5	Microporous	7.3	0.8	0.3	5
SO_4^{2-}/ZrO_2	Supported acid	–	0.3	–	–
$H_3PW_{12}O_{40}$	Heteropolyacid	–	0.9	–	–

Table 2
Reaction of toluene with TCCA over solid acids.[a]



Solid acid	Time (h)	Conversion (%)[a]	*o*/*p* ratio[a]
–	24	3	0.6
H-USY	6	100	1.0
H-BEA	24	98	1.6
H-EMT	24	98	1.2
H-MOR	48	87	1.5
H-ZSM-5	48	81.5	1.2
H-SAPO-5	48	40	3.1
SO_4^{2-}/ZrO_2	48	47.5	1.3
NAFION/MCM-41	24	98	1.4
$H_3PW_{12}O_4$	48	47.5	1.3

Conditions: $PhCH_3$:TCCA:H$^+$ (on catalyst) = 1:0.34:0.3.

[a] Determined by GC.

the presence of solid acids improves significantly the conversions and changes the *ortho*–*para* ratio in the products compared to the blank test, where no solid acid was used.

Fig. 2 (detailed results can be found in Table S1, in supporting information section) summarizes the reaction evolution with time for several solid acids. One can see that the best results are obtained with H-USY and H-EMT zeolites, which achieve the higher conversion in shorter times.

Catalysts with high surface acidity but not porous (e.g., ZrO_2/SO_4^{2-} or $H_3PW_{12}O_4$), or containing small pores (e.g. H-ZSM-5) do not exhibit good performance. On the other hand, solid with acidity and with micro- and/or mesoporosity, do show better catalytic activity. For instance, Nafion perfluorinated catalyst grafted in a MCM-41 matrix also led to high conversion (98% after 24 h). It appears therefore as a valuable chlorination catalyst for activated aromatics.

This indicates that the reaction is favored by both an appropriate pore structure and acidity. This can be due to entropic factors driving the reaction as well as the need of appropriate (strong) acidity of the solid acid. Low acidity of the catalyst, as in H-SAPO-5, also negatively influences the conversion.

In order to better understand the role of the catalyst acidity, the chlorination reaction of a more deactivated arene, chlorobenzene, with TCCA was attempted and the results are shown in Table 3. Blank tests involving only chlorobenzene and TCCA in CH_2Cl_2 or 1,2-dichloroethane do not led to any conversion after several hours at different temperatures. However, the use of acid zeolites catalyses the chlorination process and the conversion once more depends on the zeolite pore structure. Zeolites with small pores exhibit lower conversions compared to those with larger pores. For instance, H-EMT and H-USY exhibited the best conversions. In order to improve the conversion, the reaction using the H-USY and H-EMT catalysts was carried out in 1,2-dichloroethane,

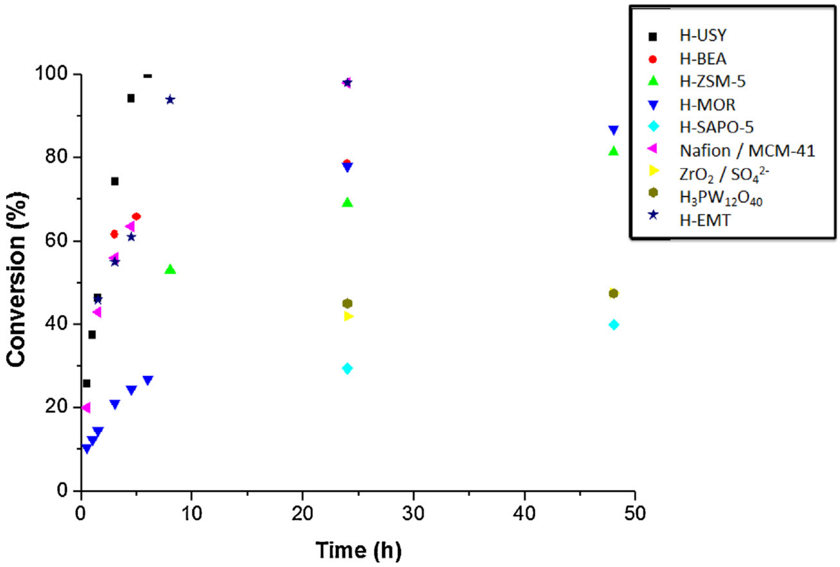
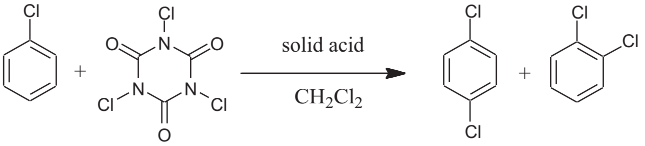


Fig. 2. Formation of o- and p-chlorotoluene as a function of reaction time and structure of the solid acid.

Table 3
Reaction of chlorobenzene with TCCA over solid acids.[a]



Solid acid	Solvent	Temp. (°C)	Time (h)	Conversion (%)[a]	*o*/*p* ratio[a]
–	CH_2Cl_2	rt	96	0	–
–	$Cl(CH_2)_2Cl$	80	24	0	–
H-ZSM5	CH_2Cl_2	rt	96	15	0.6
H-MOR	CH_2Cl_2	rt	96	27	1.1
H-EMT	CH_2Cl_2	rt	96	47	0.4
	$Cl(CH_2)_2Cl$	80	24	73	n.d.
H-USY	CH_2Cl_2	rt	96	30	0.4
	$Cl(CH_2)_2Cl$	80	24	72	0.4
H-BEA	$Cl(CH_2)_2Cl$	80	24	50	0.4

Conditions: PhCl:TCCA:H^+ (on catalyst) = 1:0.34:0.3.
[a] Determined by GC.

a solvent with higher boiling point. The increase in the temperature from room temperature to 80 °C led to an increase in the yield (ca. from 30% to 72% conversion) and shorter reaction times (from 96 h to 24 h). The *ortho–para* ratio was found to be 0.4 for the reaction of chlorobenzene with TCCA catalyzed by either H-USY (or H-EMT structure) and H-BEA contrasting with the 0.6 (*o*/*p*) value found for the reaction of this same substrate with TCCA, but in $HOAc/H_2SO_4$ (1:1) instead of HUSY [3]. Thus it appears that an acid zeolite favors the *para* position in relation to the *ortho* position, in agreement with a hindered catalyst pore shape. In contrast, H-MOR did not follow this trend and led to a ratio *ortho*/*para* = 1.1.

Nitrobenzene is not reactive with TCCA in ordinary conditions, but gave 30% conversion in the presence of H-USY zeolite. For evaluating the viability of this reaction we have carried out tests under continuous flow conditions. We have passed 0.36 mmol of nitrobenzene, pulled with a nitrogen flow of 100 mL/min over a physical mixture of TCCA and the H-USY zeolite heated to 150 °C (see Section 2). Under these conditions, a nitrobenzene conversion of nearly 53% was achieved (93% selectivity toward mono-chlorination product). Table 4 summarizes the results.

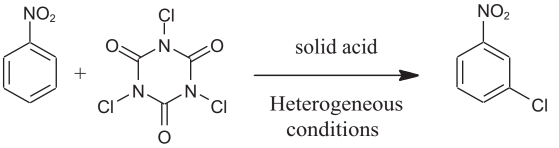
The above results support our claim that zeolites can successfully substitute liquid acids in superelectrophilic chlorination of aromatic compounds.

In order to better understand the reaction, we have employed DFT calculations at IEFPCM(H_2O)/M06-2X/6-31++G**+ECP(Si,Al,Cl) level on the reaction of TCCA with benzene catalyzed by an acid zeolite model. Computational details are given in the supporting information. We have considered the cluster T5, containing four silicon atoms and an aluminum atom as tetrahedral atoms, as a model of the zeolite active site. The acid form of the zeolite site is denominated HT5. This cluster has been shown to be large enough to mimic the local acid site properties of zeolites.

The whole process and results of the calculations are presented in Figs. 3 and 4. Firstly, all reactants (benzene, abbreviated as PhH, and TCCA) were optimized together in the presence of the model of acid site of the zeolite (HT5), in order to form the complex PhH.TCCA.HT5. Optimized geometries are shown in Fig. 3. This complex basically consists of the TCCA molecule hydrogen-bonded through the carbonyl group to the acid site (O···H distance of 1.749 Å), while benzene stays around this complex being 3.304 Å away from the nearest chlorine atom from TCCA. This adsorption step is exothermic by 15.8 kcal/mol (Fig. 4). From this structure a transition state leading to benzene ring chlorination was found (TS), with activation enthalpy of 21.8 kcal/mol, leading to a sigma complex (σ-complex 1).

This transition state has an imaginary frequency of 304*i* cm^{-1} and bond lengths $N_{TCCA}\cdots Cl$ of 2.164 Å, contrasting with the 1.691 Å found in the complex PhH.TCCA.HT5, and $Cl\cdots C_{PhH}$ of 2.094 Å, which is much smaller than the 3.304 Å calculated for the complex PhH.TCCA.HT5. IRC calculations from the transition state TS confirmed that it connects the initial adsorption complex, PhH.TCCA.HT5, to a σ-complex. This complex (σ-complex 1) was itself characterised as true minimum on the potential energy surface, since it shows no imaginary frequency after vibrational analysis, and lies 7.0 kcal/mol above the adsorption complex PhH.TCCA.HT5. This complex stays 3.603 Å from the other reactants, typical distance found for π-complexes. It has two reaction outcomes: (a) adsorption on the zeolite surface, leading to an alkoxide complex (indicated as alkoxide.DCCA (OH form) in Figs. 3 and 4), 10.5 kcal/mol (=3.5 + 7.0 kcal/mol) lower in energy in relation to σ-complex 1, but which does not lead to any product; and (b) rotation to afford σ-complex 2, in which the proton of the arenium ion is pointing toward the zeolite surface. This complex is 2.0 kcal/mol more stable than σ-complex 1, probably due to the higher proximity and better hydrogen interaction between the arenium ion and the DCCA. This complex can undergo deprotonation affording the π-complex (indicated in Figs. 3 and 4 as π-complex (OH form)) involving the product, chlorobenzene (PhCl), dichloroisocyanuric acid (DCCA) in its phenolic (OH) form and the regenerated acid site, HT5. This deprotonation is exothermic by 39.9 kcal/mol (=5.0 + 34.5 kcal/mol).

Table 4
Reaction of nitrobenzene with TCCA over H-USY zeolite.



Solid acid	Conditions	Temp. (°C)	Time (h)	Conversion (%)[a]
–	$Cl(CH_2)_2Cl$	80	120	0
H-USY	$Cl(CH_2)_2Cl$	80	24	30
H-USY	Continuous flow	150	5	53

[a] Determined by GC.

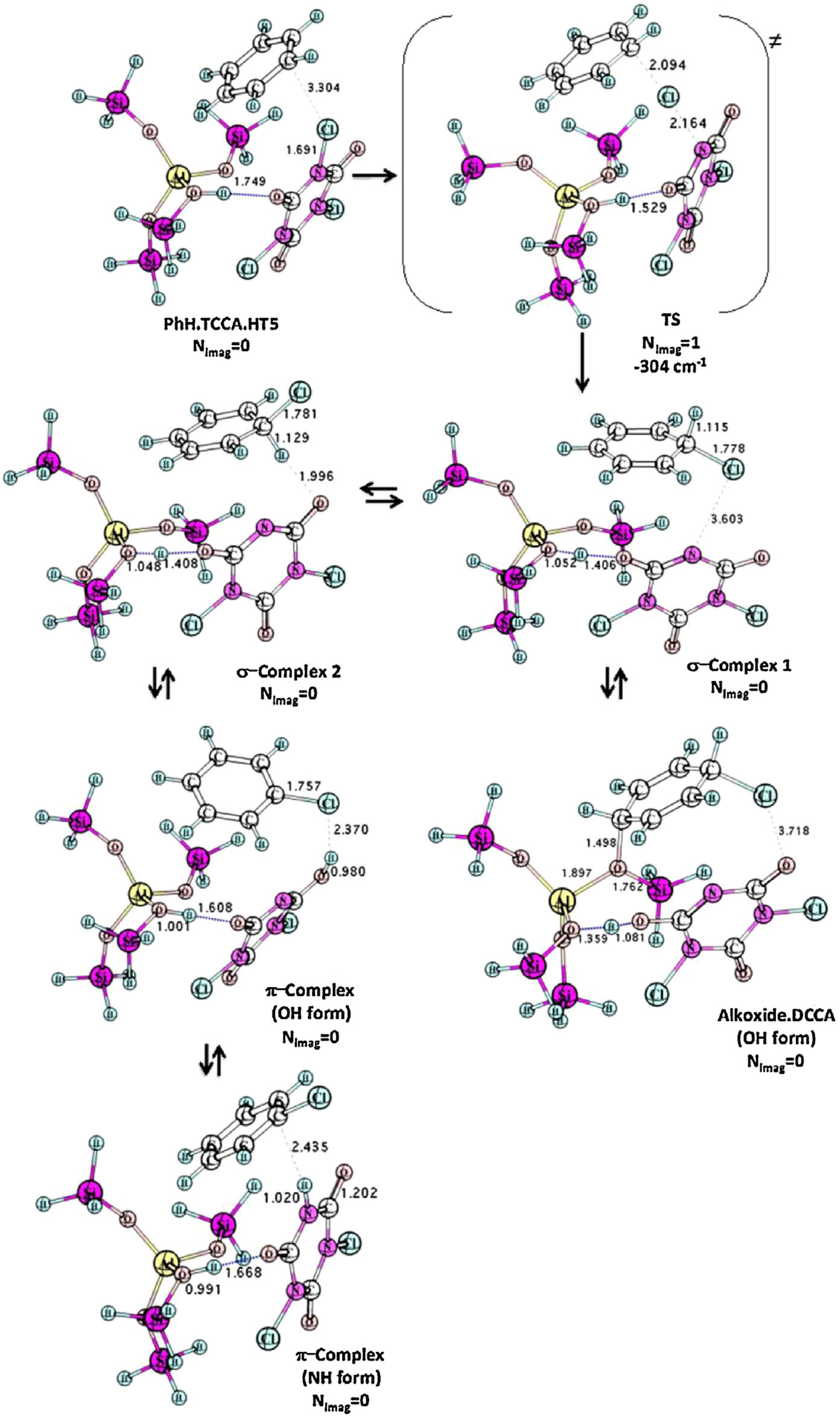


Fig. 3. Optimized geometries at IEFPCM(H_2O)/M06-2X/6-31++G**+ECP(Si,Al,Cl).

Further isomerization of this complex leads to the complex involving the imide form of DCCA (NH form), lying 9.8 kcal/mol below the energy from the OH isomer. Full dissociation of this complex in DCCA (NH isomer), PhCl and HT5 is endothermic by 19.1 kcal/mol.

Thermodynamically, the overall process is exothermic (41.4 kcal/mol) and should present an apparent enthalpy of activation of 6 kcal/mol, thus completely accessible to even occur at room temperature.

These computational results support the model of acid catalysis of TCCA toward electrophilic attack on simple aromatic rings, leading to relatively low lying apparent activation energies. Further studies on the effect of the acid strength of the zeolite, as well as its pore structure, are underway in our laboratories.
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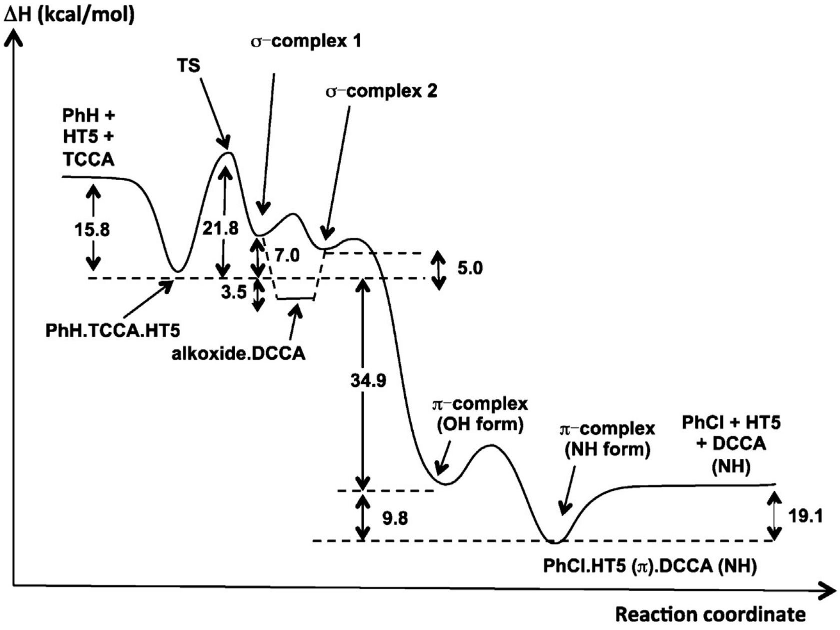

Fig. 4. Pictorial representation of the reaction coordinate for the reaction between HT5, TCCA and benzene, at IEFPCM(H_2O)/M06-2X/6-31++G**+ECP(Si,Al,Cl).

4. Conclusions

From our results, we can conclude that electrophilic chlorination of aromatic rings can be achieved by the use of cheap TCCA as chlorine source and acid zeolites. This opens up the possibilities to use this safe and easily handling reactant for superelectrophilic aromatic substitution in a heterogeneous process. This is a very interesting alternative to the strong liquid acids that we have been employing in the development of superelectrophilic chemistry of TXCA.

DFT calculations have shown that a mechanism involving protosolvated TCCA simultaneously transferring Cl^+ to the aromatic ring to afford σ-complexes, which eventually form the chlorination products, is a viable process and should present low apparent activation energies, in the order of 6 kcal/mol. This is in agreement with the observation that the reaction is taking place at relatively low temperatures with substrates such as toluene.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.04.017.

References

[1] G.A. Olah, Angew. Chem. Int. Ed. Eng. 32 (1993) 767–788.
[2] (a) D.A. Klumpp, Y. Zhang, M.J. O'Connor, P.M. Esteves, L.S. de Almeida, Org. Lett. 9 (2007) 3085–3088;
(b) G.A. Olah, D.A. Klumpp, Superelectrophiles and Their Chemistry, Wiley, New York, 2008.
[3] G.F. Mendonça, M.R. Senra, P.M. Esteves, M.C.S. de Mattos, Appl. Catal. A: Gen. 401 (2011) 176–181.
[4] L.S. de Almeida, P.M. Esteves, M.C.S. de Mattos, Tetrahedron Lett. 50 (2009) 3001–3004.
[5] R.S. da Ribeiro, P.M. Esteves, M.C.S. de Mattos, Synthesis (2011) 739–744.
[6] U. Tilstam, H. Weinmann, Org. Process Res. Dev. 6 (2002) 384–393.
[7] R.S. Ribeiro, P.M. Esteves, M.C.S. de Mattos, Tetrahedron Lett. 48 (2007) 8747–8751.
[8] L.S. de Almeida, P.M. Esteves, M.C.S. de Mattos, Synlett (2006) 1515–1518.
[9] G.F. Mendonça, A.M. Sanseverino, M.C.S. de Mattos, Synthesis (2003) 45–48.
[10] L.T.C. Crespo, R.S. Ribeiro, M.C.S. de Mattos, P.M. Esteves, Synthesis (2010) 2379–2382.
[11] G.F. Mendonça, H.C. Sindra, L.S. Almeida, P.M. Esteves, M.C.S. de Mattos, Tetrahedron Lett. 50 (2009) 473–475.
[12] L.S. de Almeida, P.M. Esteves, M.C.S. de Mattos, Synlett (2007) 1687–1690.
[13] R.S. Ribeiro, P.M. Esteves, M.C.S. de Mattos, J. Braz. Chem. Soc. 23 (2012) 228–235.
[14] R.S. Ribeiro, P.M. Esteves, M.C.S. de Mattos, J. Braz. Chem. Soc. 19 (2008) 1239–1243.
[15] G.F. Mendonça, M.C.S. de Mattos, Quim. Nova 31 (2008) 798–801.
[16] L.S. de Almeida, P.M. Esteves, M.C.S. de Mattos, Synthesis (2006) 221–223.
[17] G.F. Mendonça, R.R. Magalhães, M.C.S. de Mattos, P.M. Esteves, J. Braz. Chem. Soc. 16 (2005) 695–698.
[18] A.S.S. Sido, S. Chassaing, M. Kumarraja, P. Pale, J. Sommer, Tetrahedron Lett. 48 (2007) 5911–5914.
[19] A. Corma, Chem. Rev. 95 (1995) 559–614.
[20] K. Smith, G.A. El-Hiti, Curr. Org. Chem. 10 (2006) 1603–1625.
[21] R.A. van Santen, Chem. Rev. 95 (1995) 637–660.
[22] P. Ratnasamy, A.P. Singh, S. Sharma, Appl. Catal. A: Gen. 135 (1996) 25–55.
[23] K. Smith, G.A. El-Hiti, Green Chem. 13 (2011) 1579–1608.
[24] J.M. Gnaim, R.A. Sheldon, Tetrahedron Lett. 46 (2005) 4665–4668.
[25] B. Louis, S. Walspurger, J. Sommer, Catal. Lett. 93 (2004) 81–84.
[26] S. Walspurger, B. Louis, Appl. Catal. A: Gen. 336 (2008) 109–115.
[27] B. Louis, A. Vicente, C. Fernandez, V. Valtchev, J. Phys. Chem. C 115 (2011) 18603–18610.
[28] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 105 (2005) 2999–3093.
[29] M. Boltz, M.C.S. de Mattos, P.M. Esteves, P. Pale, B. Louis, Appl. Catal. A 449 (2012) 1–8.
[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, J.A. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.
[31] http://www.iza-structure.org/databases
[32] Y.Y. Sun, S. Walspurger, B. Louis, J.P. Tessonnier, J. Sommer, Appl. Catal. A 292 (2005) 200–207.