

ORIGINAL PAPER

DFT calculations on the Friedel–Crafts benzylation of 1,4-dimethoxybenzene using ZnCl₂ impregnated montmorillonite K10 – inversion of relative selectivities and reactivities of aryl halides

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Zinc was bound on montmorillonite K10 by cation exchange to obtain a catalyst named clayzic. In the Friedel–Crafts benzylation of 1,4-dimethoxybenzene, this catalyst was used for the synthesis of substituted diphenylmethanes using 4-chlorobenzyl chloride and 4-bromobenzyl bromide. During the reaction, sub-products from a second benzylation reaction process were observed. For a better understanding of their formation, reactions were carried out at different times to obtain data on the progress of benzylation and the relative ratio of each product was calculated using two different analytical methods. It was shown that the selectivity and reactivity of both aryl halides were reversed under these experimental conditions contrary to those obtained using the more conventional catalyst, zinc dichloride. These results were explained by geometrical and electronic considerations. It was found that the formation of transition states and Wheland intermediates from aryl bromide and chloride in the presence of clayzic can be explained in terms of preferential absorption. Moreover, the high percentage of 4-chlorobenzyl chloride conversion was attributed to its covalent radius, which is smaller than that of Br. At the same time it was shown that the presence of a Brönsted acid, due to the liberation of HCl during the benzylation, is responsible for the poisoning of the clayzic catalyst. Moreover, poisoning effect of the bromine anion could not be excluded. © 2011 Institute of Chemistry, Slovak Academy of Sciences

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Introduction

The synthesis of substituted diarylmethanes is often carried out via reductive alkylation of benzophenones or benzhydrols using triethylsilane or sodium tetrahydroborate in combination with trifluoroacetic or trifluoromethanesulfonic acid (Carey and Tremper, 1968; Gribble et al., 1977; Olah et al., 1986; Waterlot et al., 2001b). Diarylmethanes have been recently synthesized using other acids and hybrids, e.g., AlCl₃ and polymethylhydrosiloxane in various solvents such as dichloromethane, carbon tetrachlo-

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Fig. 1. Reactions of 1,4-dimethoxybenzene, I, with aryl halides, IIa and IIb, in the presence of clayzic.

ride and nitromethane (Waterlot et al., 2000a, 2001b) The authors highlighted the formation of several byproducts and the mechanisms of their formation were discussed (Waterlot et al., 2000b).

Since the late 1980's, the use of clean catalysts such as metal halides dispersed in inorganic substrates in chemical industry has grown considering environmental problems. As a consequence, superacidic sulfated zirconia (S-ZrO₂) (Yadav et al., 1993; Yadav & Thorat, 1996), zeolite (Koltunov et al., 2004; Bidart et al., 2006), silica (Miller et al., 1997, 1998; Orlovic et al., 2001), and clay (Cseri et al., 1995) catalysts have been used in the Friedel-Crafts alkylation reactions in order to substitute powerful Lewis acids such as ZnCl₂ or AlCl₃. Among these heterogeneous catalysts, zincexchanged montmorillonite K10, named clayzic (Clark et al., 1989; Cornélis et al., 1991a, 1991b), has been reported as a highly active and selective reagent for the benzylation of aromatic hydrocarbons compared with unsupported $ZnCl_2$.

From an industrial point of view, inexpensive and environmentally friendly clayzic is the right choice especially in the preparation of a variety of diarylmethanes which have found many applications in the fields of biologically active molecules, polymers, food additives and agrochemicals. Indeed, the achieved conversion of benzyl halides was about 100 % in a short time whereas both clay and ZnCl₂ require several hours to catalyze the benzylation reactions (Laszlo, 1987; Laszlo & Mathy, 1987; Clark et al., 1989); moreover, diarylmethanes were isolated with good yields and without by-products (Vanden Eynde et al., 1995).

For our research activities and in order to provide environmentally friendly chemical reactions, clean synthesis of diarylmethanes, III, was essential. The Friedel–Crafts reaction of 1,4-dimethoxybenzene, I, with halides, II, was also used as an alternative procedure (Fig. 1). Compared with all sub-products obtained during the reduction of benzophenones or benzhydrols (Waterlot et al., 2000a, 2001b), it was observed that only by-products IV and V were also formed in low yields when using a heterogeneous catalyst (Waterlot et al., 2000c). The reported chemistry of the Friedel–Crafts reaction using ZnCl₂ (Olah, 1963, 1973) and our results were compared.

To explain apparent discrepancies between the results obtained with the two catalysts and for the purpose of this study, the alkylation of 1,4dimethoxybenzene, I, was conducted using unsupported ZnCl_2 as the Lewis acid catalyst and ZnCl_2 exchanged montmorillonite K10 clay following the procedure described in a previous study (Waterlot et al., 2000c). For both these catalysts, reactions were performed in triplicates, at different times, in order to obtain data on the alkylation progress. In this contribution, results of these experiments are reported and the reactivity of aryl halides in the presence of clayzic using the density functional theory (DFT) calculations is explained.

Experimental

For each data point, Friedel–Crafts reactions were carried out in triplicates. Analyses were performed on a Varian 5000 HPLC chromatograph with a multi-wavelength UV-VIS detector (Varian, Essonne, France) under reversed-phase conditions (octadecylbonded silica column, Supelco France, S^t-Germain-en-Laye, France) using acetonitrile–water ($\varphi_r = 6 : 4$, Acros Organics, Noisy-le-Grand, France) as the mobile phase. NMR spectra were run on a Bruker AC300 spectrometer (Marne-la-Vallée, France) at 300 MHz for ¹H and 75 MHz for ¹³C, using CDCl₃ (Acros Organics, Noisy-le-Grand, France) as a solvent and tetramethylsilane (Acros Organics,) as an internal standard. Chemical shifts (δ) are reported in parts per million. Spectroscopic data and elemental analyses were described in detail in previous studies (Waterlot et al., 2000c, 2001b). The treatment of each mixture was carried out following the procedure described below. The relative ratio of compounds I, III, IV, and V was determined using HPLC after the determination of the retention time related to each compound and establishment of the calibration curves. These compounds were characterized by the wavelength (λ/nm) at which absorption occurs (Table 1). In addition, ¹H NMR spectra were performed for each mixture and the relative ratio was determined on basis of the ¹H NMR signals of methoxy groups (Table 1).

1,4-Dimethoxybenzene (1 g, 7.24 mmol, Sigma– Aldrich, Saint–Quentin–Fallavier, France) in dichloromethane (5 mL, Acrōs Organics, Noisy-le-Grand, France) was added to a stirred solution of 4-bromobenzyl bromide, *IIa*, or 4-chlorobenzyl chloride, *IIb* (7.24 mmol, Sigma–Aldrich), and ZnCl₂ (1.46 g,

Table 1. Chemical parameters used in HPLC (λ /nm) and ¹H NMR (δ) for the determination of the relative ratio of compounds I, III, IV, and V

Parameter	Ι	IIIa	IIIb	IVa	IVb	Va	Vb
$\lambda/\mathrm{nm} \over \delta$	$196, 228, 290 \\ 3.80$	$\begin{array}{c} 198, 224, 292\\ 3.75, 3.78 \end{array}$	$\begin{array}{c} 198,224,292\\ 3.74,3.76\end{array}$	$198,218,296\\3.69$	198, 218, 296 3.70	$\begin{array}{c} 198,\ 224,\ 286\\ 3.56,\ 3.66\end{array}$	$198,224,286\\3.57,3.67$

Table 2. Benzylation of 1,4-dimethoxybenzene using $ZnCl_2$ as the catalyst

Entry	Aryl halides	t	III	IV	V	Ι	Conversion of II
		h		%	a		%
1	IIa	118	29	5	0	66	39
2	IIb	118	28	2	0	70	32
3	IIa	142	33	6	1	60	47
4	IIb	142	36	3	0	62	42
5	IIa	166	37	7	2	54	55
6	IIb	166	37	5	2	56	51
7	IIa	312	54^{b}	11^{b}	10^b	25	96
8	IIb	312	60^b	9^b	7^b	24	92

a) Yields were determined by ¹H NMR and HPLC; b) isolated yields.

Table 3. Benzylation of 1,4-dimethoxybenzene using clayzic as the catalyst

Entry	Aryl halides	t	III	III	V	Ι	Conversion of II
		h		%	%		
1	IIa	19^b	54^c	3^c	2^c	41	64
2	IIb	19^{b}	49^c	16^{c}	4^c	31	89
3	IIa	24	52^c	8^c	5^c	35	78
4	IIb	24	49^c	15^c	6^c	30	91
5	IIa	30	52^c	10^c	6^c	32	84
6	IIb	30	49	15	7	29	93
7	IIa	$48^{b,d}$	42	17	12	24	100
8	IIb	48	48^c	17^c	7^c	26	96
9	IIa	$96^{b,d}$	48	18	8	24	100

a) Isolated yields; b) the same results as in Waterlot et al. (2000c); c) yields determined by ¹H NMR and HPLC; d) quantitative conversion of aryl halides.

1.08 mmol, Sigma–Aldrich) in dichloromethane (5 mL). The mixture was stirred at room temperature for the required time. Then, the reaction was guenched with water (50 mL). After stirring, the organic layer was extracted with dichloromethane $(2 \times 10 \text{ mL})$, dried over CaCl₂ and concentrated under vacuum. Benzylation of 1,4-dimethoxybenzene with clayzic was conducted following the procedure described in detail by Waterlot et al. (2000c). This catalyst was prepared following the general procedure described by Clark et al. (1992) and Clark (1994) with slight modifications. $ZnCl_2$ (10 g) and montmorillonite K10 (60 g, Sigma–Aldrich) were added to dry methanol (100 mL, Acros Organics). The resulting slurry was stirred at room temperature for 5 hours forming a clay which was then filtered and washed with dichloromethane (30 mL, Acros Organics). The resulting powder was thermally activated overnight at 120 °C (Cornélis et al., 1991b; Phukan et al., 2003).

Results and discussion

In course of the process requiring the use of diarylmethanes, IIIa and IIIb, to produce a redox polymer (Waterlot et al., 2001a, Waterlot & Couturier, 2010), differences between our results using unsupported ZnCl₂ and ZnCl₂ exchanged montmorillonite K10 clay were examined. A systematic study was carried out with the two catalysts in order to understand the preliminary results.

Benzylation of 1,4-dimethoxybenzene, I, with aryl halides IIa and IIb was first conducted with ZnCl₂. In this reaction, 2,5-dimethoxy-l-(4'-halobenzyl)benzene, III, was produced and dibenzylated derivatives from a second benzylation reaction appeared (Fig. 1). The *p*-isomer, IV, was formed selectively after 144 hours. At a longer reaction time, *m*-isomer, *V*, was detected, and at the end of the reaction, *m*- and *p*-isomers were isolated in similar yields (Table 2).



Fig. 2. *p*-Dibenzylated derivatives/*m*-dibenzylated derivatives molar ratio (-IVa/Va; -IVb/Vb) after various reaction times: A) using ZnCl₂ as catalyst; B) using clayzic.



Fig. 3. Conversion of aryl bromide, IIa (\Box), and aryl chloride, IIb (\bigcirc): A) using ZnCl₂ as the catalyst; B) using clayzic. Average values (n = 3) and standard deviation are given.

Regarding the results in Tables 2 and 3, the selectivity of clayzic used as the catalyst was different than that of ZnCl₂ at the beginning, during and at the end of the reaction. For instance, it is undeniable that the time required for total conversion of aryl halides using clayzic (Table 3, entries 7 and 9) is shorter than that obtained using ZnCl₂ (Table 2, entries 7 and 8). Moreover, second benzylation occurred in the presence of clayzic earlier than with ZnCl₂. These results can be explained by the high local concentration of Zn²⁺ within the pores of montmorillonite creating a high activated region towards incoming alkyl halide derivatives.

As shown in Fig. 2, selectivity of the second benzylation resulting in m- and p-isomers, IV and V, relies on the nature of the catalyst and the benzyl halide, IIaor IIb. As a consequence, the conversion rate of benzyl halides depends on the Lewis catalyst (Fig. 3). In our experiments, reaction rates of 4-bromobenzyl bromide, IIa, and 4-chlorobenzyl chloride, IIb, are very similar when using ZnCl₂ (Fig. 3a). Therefore, there is no significant difference between the activities of the aryl halides studied up to 118 hours. After this reaction time, the conversion rate of aryl bromide, IIa, became significantly faster than that of aryl chloride, IIb, as reported in previous studies (Olah, 1973; Laszlo, 1987; Laszlo & Mathy, 1987). In contrast, differences in terms of activity occurred when clayzic was used. Reactivity of aryl chloride was higher than that of bromide after the reaction beginning. Twenty hours after the beginning of the reaction, 90 % of the initial amount of aryl chloride were consumed whereas 63 % of the amount of aryl bromide were used for the benzylation of 1,4-dimethoxybenzene. After this time, conversion of aryl chloride, *IIb*, was almost stopped. In contrast, total conversion of aryl bromide, *IIa*, was achieved after 40 hours of the reaction.

It is well-known that major structural changes occur in montmorillonite K10 during its activation at higher temperatures. In our experiments, thermal treatment of the ZnCl₂/montmorillonite K10 catalyst was carried out at 120 °C overnight. Under these conditions it was shown that the basal spacing of our catalyst is high (Choudhari & Mantri, 2002; Phukan et al., 2003). In contrast, activity of the acid sites activated at 120 °C was lower than of those activated at higher temperatures. With regard to the activation procedure of our heterogeneous catalyst, the exchange of Zn²⁺ ions for the exchangeable cations of montmorillonite K10 can occur. During the activation of the catalyst at 120 °C, loss of water from the interstitial spaces of the clay was limited, reflecting a little de-



Fig. 4. Mechanism of 1,4-dimethoxybenzene (I) benzylation.



Fig. 5. Schematic forms of two possible transition states with hexacoordinated zinc.

crease of its Brönsted acidity. Furthermore, formation of bonds between physically absorbed ZnCl₂ and clay can take place creating new active sites, which is followed by the realease of the HCl gas. However, this phenomenon seems to be limited at 120 °C (Choudhary & Mantri, 2002). High reactivity of aryl bromide in the presence of clayzic can be also explained by the highly polar clayzic pores into which the more polar or polarizable substrate diffuses (Clark et al., 1994). Obviously, this phenomenon does not explain the obtained results.

Benzylation scheme of 1,4-dimethoxybenzene, I, is shown in Fig. 4 and it follows the general mechanism of the Friedel–Crafts alkylation.

If the reaction proceeds through a carbocationic intermediate, theory predicts that relative reactivity of alkyl halides is dictated by the catalytic activity, the Lewis acid (Clark & Macquarrie, 1996), the structure of the halide reagent and the energy of the halogen carbon bonds (Price, 1947; Olah, 1973). In the experiments conducted with clayzic, aryl halides can be absorbed on the catalyst to produce carbenium ions, involving the steric properties of aryl halides *IIa* and *IIb*. Therefore, at the beginning of the reaction, high conversion rate of 4-chlorobenzyl chloride, *IIb*, can be explained by the low covalent radius of Cl compared to that of Br of 4-bromobenzyl bromide, *IIa*.

Based on the results related to the paradoxical selectivity of the Friedel–Crafts benzylation using commercial clays (Choudhary & Jana, 2002), a redox mechanism for the activation of benzyl chloride to produce the carbocationic intermediate *IIc* in the presence of clayzic was proposed. Similar mechanisms were proposed for other heterogeneous catalysis and other metal salts (Cseri et al., 1995; Choudhary & Jana, 2001; Singh et al., 2004; Bachari & Cherifi, 2007; Choudhary & Jha, 2008). Formation of a chlorine radical, much more reactive than the bromine one, can also explain the high conversion rate of 4-chlorobenzyl chloride after the beginning of the reaction up to 19 hours of its duration.

Even if the formation of a hexacoordinated sphere is less evident with the Zn^{2+} heterogeneous catalyst than with other metal-composites (Ahmed & Dutta, 2005), the high conversion of 4-chlorobenzyl chloride up to the reaction time of 19 hours can be explained by a possible chelation of this compound and 1,4dimethoxybenzene with the presence of two catalytic acid sites, Brönsted and Lewis, of clayzic (Fig. 5). In schematic form, the transition state C2 seems to be more suitable due to the Brönsted activity of our catalyst. As reported by Cornélis et al. (1993), formation of this transition state can occur in two steps: i) attack by the aryl halides, bromine or chlorine, on the zinc Lewis acid already coordinated to 1,4dimethoxybenzene due to the low temperature of the reaction (Barlow et al., 1993); ii) Brönsted acid catalysis of the leaving halide due to the superacidic clay surface, with the acidity of the remaining water molecules enhanced through their coordination to zinc.



Fig. 6. Schematic forms of possible transition states with hexacoordinated zinc.



Fig. 7. Representation of the HOMO (in grey) and the LUMO (gridded) orbitals of 2,5-dimethoxy-1-(4'-bromobenzyl)benzene, IIIa, and 2,5-dimethoxy-1-(4'-chloro-benzyl)benzene, IIIb.

In the second alkylation, possible simultaneous chelation of diarylmethanes *IIIb* or *IIIa*, and aryl halides *IIb* or *IIa* with already coordinated zinc can be considered (Fig. 6). Regarding the properties of the chlorine atom (i.e., electronegativity and covalent radius), the formation of transition states C3 and C4 is easier when X = Cl than when X = Br. This might explain the consumption of 4-chlorobenzyl chloride up to the reaction time of 19 hours and the higher amount of the (*p*- and *m*-) isomers *IVb* and *Vb* than that of the (*p*- and *m*-) isomers *IVa* and *Va*.

To understand the formation of by-products IVand V, geometries and electronic parameters of compounds I, II, and III were optimized using DFT calculations (the Gaussian base used was 6.31 G** with s, p orbital for hydrogen atoms and s, p, and d orbitals for the others atoms 6.31 G**), by means of the Jaguar programs (Schrödinger, Inc. 1991–2000; Friesner, 1991) and SPARTAN optimized using the semiempirical AM1 method (Dewar et al., 1985; Wavefunction Inc., 1999).

Energy of the lowest unoccupied molecular orbital (LUMO) of each aryl halide, IIa and IIb, is noticeably lower than that of compounds I and III for which the highest occupied molecular orbital (HOMO) energies are the highest and in the same order of magni-

 Table 4. Energies of HOMO and LUMO orbitals obtained by

 DFT calculations

Compound	Ι	IIa	IIb	IIIa	IIIb	
Orbital energy		ŀ	$J \text{ mol}^{-1}$			
HOMO LUMO	$\frac{-825}{37}$	$\begin{array}{c} -925 \\ -41 \end{array}$	$-927 \\ -25$	$\begin{array}{c} -836\\11\end{array}$	$-833 \\ 14$	

tude (Table 4). As a consequence, LUMO orbital of the aryl halides approached the HOMO orbital of 1,4dimethoxybenzene, *I*. Competition between the first and the second alkylation can be explained by the nearly equal HOMO energies of diarylmethanes *IIIa* and *IIIb* and 1,4-dimethoxybenzene, *I*.

Graphical representations of the HOMO and LUMO orbitals of *IIIa* and *IIIb* are shown in Fig. 7. HOMO positions of these compounds indicate that the second alkylation takes place on the 1,4-dimethoxybenzene group.

The distribution of isomers varied significantly with the reaction time reaching the thermodynamic equilibrium after 48 hours (Table 3, Fig. 2b). On the other hand, selectivity of the second alkylation of *IIIb*



Fig. 8. Structure of compounds III-V determined by calculations of the C—C lengths and angles.



Fig. 9. Mechanism of diarylmethanes (III) benzylation with clayzic as the catalyst.

seemed to be higher than that of *IIIa* in particular in the first 19 hours of the reaction time. Interestingly, stabilization of the aryl chloride, *IIb*, conversion occurred at the same time (Table 3, Fig. 2b). These results suggest that the release of HCl during the Friedel–Crafts alkylation contributes to the significant decrease of the clayzic activity. As a consequence, HCl can be considered as a poison to the clayzic catalyst.

Theoretical investigations on the formation of di-substituded 1,4-dimethoxybenzene in presence of clayzic

Friedel–Crafts reactions of diarylmethanes IIIa and IIIb with aryl halides IIa and IIb, respectively, were investigated from a theoretical point of view. The mechanism described in Fig. 6 was considered and the C— C lengths (d) and angles (α) (Fig. 8) of compounds III–V, and of the Wheland intermediates (Wheland, 1942; Tyagi & Yadav, 1990) VIa and VIb (Figs. 8 and 9) were determined.

As reported in Table 5, the comparison of lengths and angles of bromide and chloride compounds with those of their Wheland intermediates did not show large differences. Hence, these considerations did not explain the previous results. The total energy values for geometry optimized structures energy of each compound and their Wheland intermediates were then calculated taking into account the partial positive charge on the aromatic ring.

A reaction coordinate diagram for each electrophilic aromatic substitution was thus obtained (Figs. 10 and 11). The first diagram indicates that the stability of products IIIa and IIIb is lower than that of 1,4-dimethoxybenzene, I, (Fig. 10) implying that changes of the Gibbs free energy (ΔG°) related to the monobenzylation is endergonic. According to the Hammond postulate, Wheland complexes derived from the methoxylated intermediate are formed via late transition states. For this monobenzylation reaction, the energy of the Wheland intermediate was 106.7 kJ mol⁻¹ for *IIIa* and 84.9 kJ mol⁻¹ for *IIIb*, showing high stability of intermediate VIIb in comparison with VIIa. As a consequence, the formation of intermediate compound *IIIb* was more favorable than that of *IIIc* and so, obviously, monobenzylation of 1,4dimethoxybenzene conducted with aryl bromide, IIa, was slower than that with aryl chloride, *IIIb* (Table 3, entries 1, 2 and 3, 4).

The energy coordinate diagram for the benzylation of *IIIa* and *IIIb* with aryl halides *IIa* and *IIb* was then considered. As reported in Fig. 11, the endproducts have higher energies than the starting products, reflecting that these reactions are endergonic too.

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Table 5. Structural characteristics, energy of compounds III-V, and of their corresponding Wheland transition

Compound	d_1	d_2	d_3	D_4	α_1	α_2	E	
		Å	L		0		$kJ mol^{-1}$	
IIIa	1.491	1.492	-	-	112.65	-	51.94	
IIIb	1.492	1.491	-	-	112.56	-	51.32	
VIa	1.486	1.542	_	_	111.21	-	106.71	
VIb	1.486	1.542	-	-	111.19	-	84.86	
IVa	1.492	1.491	1.491	1.492	112.56	112.56	80.55	
IVb	1.491	1.491	1.491	1.491	112.67	112.67	79.29	
VIIa	1.493	1.489	1.542	1.486	110.94	111.19	133.13	
VIIb	1.493	1.489	1.542	1.486	110.92	111.22	108.43	
Va	1.515	1.516	1.516	1.515	116.20	116.20	85.12	
Vb	1.513	1.513	1.513	1.513	113.56	113.56	83.40	
VIIIa	1.488	1.494	1.542	1.486	114.12	111.20	137.93	
VIIIb	1.488	1.495	1.543	1.485	114.44	114.44	114.88	



Reaction coordinate

Fig. 10. Energy coordinate diagram for the monobenzylation of 1,4-dimethoxybenzene, I.



Fig. 11. Energy coordinate diagram for the benzylation of diarylmethanes IIIa and IIIb with aryl halides IIa and IIb, respectively.

Furthermore, p-isomers IV are more stable than misomers V due to some steric effects which is in accordance with the theory. Interestingly, there are no important differences between the energy of the Wheland intermediates associated to the chloride ($\Delta = 6.4$ kJ mol⁻¹) and bromide isomers ($\Delta = 4.8$ kJ mol⁻¹). In contrast, significant differences in the Wheland intermediates energy between arenium chloride ions and arenium bromide ions were observed. Finally, it is interesting to note that the transition-state energies necessary to obtain Wheland intermediates VIIb and VI-IIb are lower than those for VIIa and VIIIa. These results explain why the combined yield of the dibenzylated products IVb and Vb, obtained by a reaction of *IIIb* with any chloride *IIb*, is higher than that of brominated compounds IVa and Va (Table 3, entries 1 and 2, 3 and 4, 5 and 6).

From our results on the first and second benzylation of 1,4-dimethoxybenzene, *I*, using clayzic as the catalyst it seems that 4-chlorobenzyl chloride, *IIb*, reacts faster than 4-bromobenzyl bromide, *IIa*. This is in accordance with the conversion rate of halides at the beginning of the reaction and up to 19 hours (Fig. 3b). After this time, the release of HCl, related to the mechanism of the Friedel–Crafts benzylation, was more significant than that of HBr at the same reaction time (Fig. 3b). As the acid treatment of montmorillonite K10 increases its reactivity (Olah, 1963; Tyagi & Yadav, 1990; Pai et al., 1997; Rhodes et al., 1991), reduction of the catalyst activity can be attributed to the counter ion of the acid (Chouday at al., 1991; Vanden Eynde at al., 1995). Poisoning mechanism of the clayzic catalyst was also shown to be due to HCl formation during the Friedel–Crafts benzylation. However, from this comparative study of the benzylation using chloride or bromide derivatives, poisoning effect of the bromine anion cannot be excluded.

Conclusions

This study allows a better understanding of the role of clayzic as the catalyst in comparison with ZnCl_2 in the course of the 1,4-dimethoxybenzene benzylation with aryl halides. Using density functional theory calculations it was shown that the higher percentage of 4-chlorobenzyl chloride conversion, compared to that of 4-bromobenzyl bromine, was due to the high stability of the transition states of chloride, and smaller covalent radius of Cl compared to that of Br. Thus, the mechanism related to the poisoning of clayzic due to the release of HCl led to total conversion of aryl bromide prior to aryl chloride.

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