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In situ spectroscopic studies related to the mechanism of the Friedel–Crafts acetylation of benzene in ionic liquids using $AlCl_3$ and $FeCl_3$ †

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Received 11th October 2001, Accepted 14th November 2001

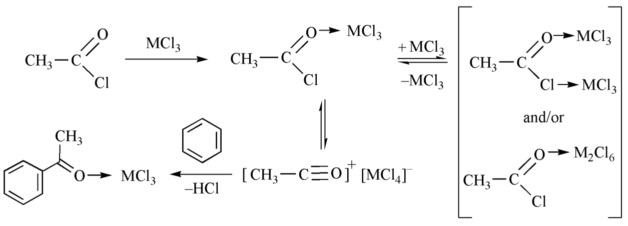
Several aspects of the mechanism of the Friedel–Crafts acetylation of benzene were studied by *in situ* spectroscopic methods in ionic liquids, prepared from MCl_3 (M = Al or Fe) and 1-butyl-3-methylimidazolium chloride ([bmim]Cl). Mössbauer measurements have revealed that the addition of $FeCl_3$ to [bmim]Cl leads to an equilibrium mixture that contains solid $FeCl_3$, [bmim][Fe_2Cl_7], and Fe_2Cl_6 and/or [bmim][$FeCl_4$], depending on the molar ratio of $FeCl_3$ and [bmim]Cl. The formation of $[(CH_3CO)_2CHCO]^+[MCl_4]^-$, a potential side product in the Friedel–Crafts acetylation of benzene, was shown to require the presence of both the acetylium ion $[CH_3CO]^+[MCl_4]^-$ and free acetyl chloride. We have confirmed that $[(CH_3CO)_2CHCO]^+[MCl_4]^-$ does not involve in the Friedel–Crafts acetylation of benzene. Experimental data and theoretical calculations indicate that the acetylium ion $[CH_3CO]^+[MCl_4]^-$ is the key intermediate in the Friedel–Crafts acetylation of benzene and the reaction proceeds through an ionic mechanism.

Introduction

The elimination or replacement of hazardous and volatile organic solvents in industrial processes is one of the key objectives of green chemistry.[1] Since the application of solvent free processes could not always be possible due to the intrinsic nature of the chemistry involved, a wide range of alternative solvents have been utilized including water,[2] alcohols,[3] ionic[4] and fluorous[5] media as well as supercritical liquids.[6]

Friedel–Crafts acylation of aromatic compounds has been widely utilized in the production of pharmaceuticals and fine chemicals for more than a century.[7] Several mechanisms[8] have been proposed based on *in situ* IR[9] and NMR measurements.[10] Some of the key intermediates have been prepared[9c,d] and structurally characterized.[11] Since most of the conventional industrial processes utilize volatile and hazardous halogenated solvents, their replacement with ionic liquids could considerably lower the environmental risks involved.

Although various Friedel–Crafts reactions have already been performed using ionic liquids,[12,13] only our *in situ* IR studies have addressed some of the key mechanistic questions using two kinds of ionic liquids prepared from [bmim]Cl and $AlCl_3$ or $FeCl_3$, respectively.[14] We have shown that the Friedel–Crafts acetylation of benzene in the presence of MCl_3 (M = Al or Fe) in [bmim]Cl proceeds through several intermediates including the MCl_3 adduct of the acetyl chloride ($CH_3CClO{\longrightarrow}MCl_3$),[9a,b,15,16a,b] the complex of acetyl chloride and two MCl_3,[9a,b,16a,b,17] and the acetylium ion $[CH_3CO]^+$-$[MCl_4]^-$,[9a,11a,17] to yield the final product, the MCl_3 adduct of acetophenone[18] (Scheme 1). Since the same intermediates were observed in 1,2-dichloroethane, we have concluded that the mechanism of the Friedel–Crafts acetylation of benzene is exactly the same in ionic liquids as that in 1,2-dichloroethane.[14] It was also confirmed that the acetylium cation $[CH_3CO]^+$-$[MCl_4]^-$ (M = Al or Fe) is the key intermediate in the Friedel–Crafts acetylation reactions of benzene in these ionic liquids. It should be noted that in the *absence of benzene* the formation of $[(CH_3CO)_2CHCO]^+[MCl_4]^-$ could take place.[9d,e,14] Since this species could lower the atom economy of the Friedel–Crafts acetylation of aromatics, we have now investigated the mechanism of its formation.



Scheme 1

While it is known that the addition of $AlCl_3$ to [bmim]Cl leads to an equilibrium mixture of $AlCl_3$, $[bmim]^+[AlCl_4]^-$, and $[bmim]^+[Al_2Cl_7]^-$,[13] no structural information is available for $FeCl_3$ containing ionic liquids.[12d] We also report here the results of the first Mössbauer spectroscopic characterization of ionic liquids prepared from $FeCl_3$ and [bmim]Cl.

Results and discussion

The formation of $[(CH_3CO)_2CHCO]^+[MCl_4]^-$

We have already shown that the reaction of a five fold excess of acetyl chloride with $AlCl_3$ in 1,2-dichloroethane resulted in the instantaneous appearance of the MCl_3 adduct of the acetyl

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† Based on the presentation given at Dalton Discussion No. 4, 10–13th January 2002, Kloster Banz, Germany.

DOI: 10.1039/b109303g

chloride ($CH_3CClO{\longrightarrow}AlCl_3$), followed by the slow formation of the complex of acetyl chloride and two $AlCl_3$, and $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$.[14] It has been suggested that the latter forms *via* the trimerization of the acetylium ion $[CH_3CO]^+[AlCl_4]^-$.[9d,e] The proposed mechanism involves proton abstraction from the acetylium ion $[CH_3CO]^+[AlCl_4]^-$ by the $[AlCl_4]^-$ anion to yield $HAlCl_4$ and ketene, $CH_2{=}C{=}O$ [eqn. (1a)],

$$[CH_3CO]^+[AlCl_4]^- \rightleftharpoons CH_2{=}C{=}O + HAlCl_4 \tag{1a}$$

$$HAlCl_4 \rightleftharpoons HCl + AlCl_3 \tag{1b}$$

which in turn, reacts with another acetylium ion to form $[CH_3COCH_2CO]^+[AlCl_4]^-$. Proton abstraction from the latter species by the $[AlCl_4]^-$ anion results in $HAlCl_4$ and another ketene intermediate, $CH_3COCH{=}C{=}O$, which reacts with an acetylium ion to form $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$. If this mechanism is correct and $[CH_3CO]^+[AlCl_4]^-$ is observable in solution, the formation of $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$ is expected to proceed. However, when 17 mmol acetyl chloride is reacted with 45 mmol $[bmim]^+[Al_2Cl_7]^-$, $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$ does not form (Fig. 1). After the addition of acetyl chloride, its concentration decreased so fast that, after 5 minutes (the second spectrum in Fig. 1), the band at 1800 cm^{-1} for acetyl chloride could not be observed as it was converted to the $AlCl_3$ adduct of the acetyl chloride ($CH_3CClO{\longrightarrow}AlCl_3$) (band B at 1644 cm^{-1}) and the acetylium ion $[CH_3CO]^+[AlCl_4]^-$ (band D at 2300 cm^{-1}). The complex of acetyl chloride and two $AlCl_3$ (band C at 1571 cm^{-1}) is formed more slowly at the expense of the $CH_3CClO{\longrightarrow}AlCl_3$, as expected.

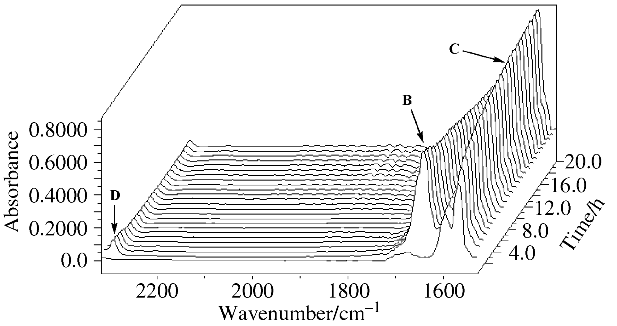


Fig. 1 *In situ* IR spectra of the reaction of 17 mmol acetyl chloride with 45 mmol $[bmim]^+[Al_2Cl_7]^-$.

A band at 2200 cm^{-1} (E), due to $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$, cannot be observed at all. More importantly, the absorbance value of band D did not change in 20 hours indicating that "self" trimerization of the acetylium ion $[CH_3CO]^+[AlCl_4]^-$ cannot be responsible for the formation of $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$. Thus, free acetyl chloride must play a key role in the formation of $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$. This was confirmed by monitoring the addition of 101.4 mmol acetyl chloride in eight equal portions to 50.7 mmol $[bmim]^+[Al_2Cl_7]^-$ (Fig. 2). The formation of $CH_3CClO{\longrightarrow}AlCl_3$ and the acetylium ion $[CH_3CO]^+[AlCl_4]^-$ is again so fast during the addition of the first three portions that free acetyl chloride cannot be observed. When the total amount of acetyl chloride is higher than one equivalent, the formation of $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$ begins and the concentration of $CH_3CClO{\longrightarrow}AlCl_3$ and $[CH_3CO]^+[AlCl_4]^-$ decreases slowly (Fig. 3).

We have recently shown that the reaction of acetyl chloride with $FeCl_3$ in [bmim]Cl at room temperature results in the formation of the $FeCl_3$ adducts of acetyl chloride, the acetylium ion $[CH_3CO]^+[FeCl_4]^-$, and $[(CH_3CO)_2CHCO]^+[FeCl_4]^-$.[14] When the same experiment was performed at 0 °C, the formation of the latter could not be observed while the acetylation of benzene proceeds leading to the $FeCl_3$ adduct of acetophenone. This result confirms that $[(CH_3CO)_2CHCO]^+[FeCl_4]^-$ is a side product, just like in the case of the $AlCl_3$ containing systems.

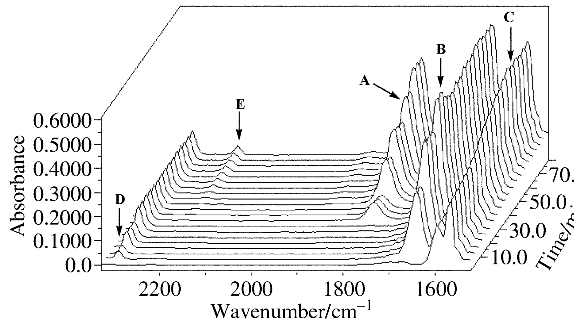


Fig. 2 *In situ* IR spectra of addition of 101.4 mmol acetyl chloride in eight equal portions to 50.7 mmol $[bmim]^+[Al_2Cl_7]^-$.

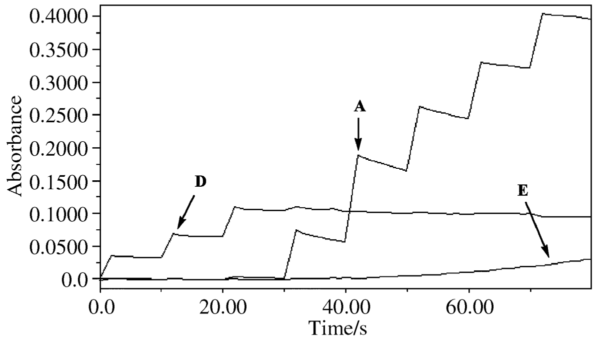
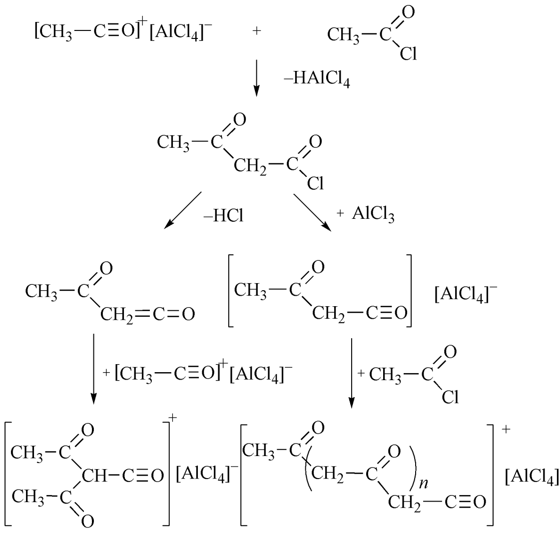


Fig. 3 Absorbance profile of the bands at 1800 cm^{-1} (A: CH_3COCl), 2200 cm^{-1} (E: $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$), and 2300 cm^{-1} (D: $[CH_3CO]^+[AlCl_4]^-$).

Based on these results we propose that the free acetyl chloride could either serve as the scavenger for $AlCl_3$ in eqn. (1b). or could undergo acetylation by the acetylium ion $[CH_3CO]^+[AlCl_4]^-$ resulting in CH_3COCH_2COCl. The latter could eliminate HCl to form a ketene intermediate, $CH_3COCH{=}C{=}O$, which could undergo rapid acetylation by $[CH_3CO]^+[AlCl_4]^-$ yielding $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$ (Scheme 2). Alternatively, the reaction of CH_3COCH_2COCl with free $AlCl_3$ could result in a new acylium ion $[CH_3COCH_2CO]^+[AlCl_4]^-$, which could react further to yield higher oligomers.



Scheme 2

Finally, the possible role of $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$ in the formation of the $AlCl_3$ adduct of acetophenone was also

Table 1

	Mole ratio		Spectral component		
	bmimCl	$FeCl_3$	Doublet 1	Doublet 2	Singlet
A	1	2			
δ/mm s^{-1}			0.30	0.33	0.58
Δ/mm s^{-1}			0.33	1.30	na
Mole ratio			0.41	0.40	0.20
B	1	1			
δ/mm s^{-1}			0.29	0.35	0.54
Δ/mm s^{-1}			0.23	1.22	na
Mole ratio			0.80	0.15	0.05
C	1.5	1			
δ/mm s^{-1}			0.33	0.34	
Δ/mm s^{-1}			0.24	1.24	
Mole ratio			0.53	0.48	

investigated. After the addition of acetyl chloride (40.8 mmol) to a solution of $AlCl_3$ (40.8 mmol) and [bmim]Cl (20.1 mmol) at 0 °C, the formation of $CH_3CClO{\longrightarrow}AlCl_3$ (band B) and $[CH_3CO]^+[AlCl_4]^-$ (band D) could be clearly seen and the bands assigned to $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$ were not observable, even after 60 minutes (Fig. 4). However, when benzene was added to the solution the bands B and D disappeared immediately, band A decreased extremely slowly, and bands F and G, assigned to the $AlCl_3$ adduct of acetophenone, appeared concomitantly to the disappearance of band A. The fact that the acetylation proceeds even in the absence of $[(CH_3CO)_2CHCO]^+$-$[AlCl_4]^-$ indicates that it is a side product. Thus, performing the reaction at low temperature could increase the atom economy of the Friedel–Crafts acylation reactions. If the reaction rate significantly decreases at lower temperatures, the step-wise addition of the acid chloride to the solution of the aromatics in ionic liquid could also result in higher atom economy. Not surprisingly, textbook procedures for Friedel–Crafts acylation recommend the drop-wise addition of acid chlorides to the aromatics.

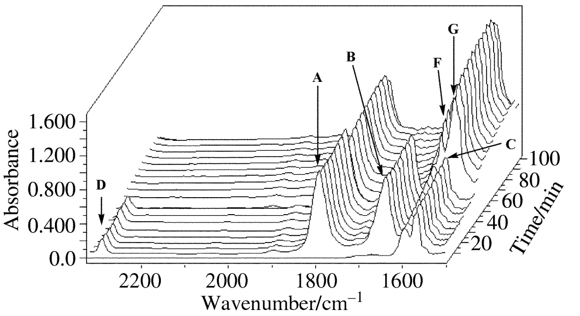


Fig. 4 *In situ* IR spectra of the Friedel–Crafts acetylation of 44.9 mmol benzene with 40.8 mmol acetyl chloride in the presence of 40.8 mmol $AlCl_3$ in 20.1 mmol [bmim]Cl at 0 °C.

Structural characterization of $FeCl_3$ containing ionic liquids

In order to obtain structural information on the $FeCl_3$ containing ionic liquid, we have measured the Mössbauer spectra of three different ionic liquids using the molar ratios of 1 : 2 (sample **A**), 1 : 1 (sample **B**), and 1.5 : 1 (sample **C**) between [bmim]Cl and $FeCl_3$, respectively (Table 1, **A**: Fig. 5, **B**: Fig. 6, **C**: Fig. 7).

The Mössbauer spectra of samples **A** and **B** contain three components. The two major components are doublets 1 and 2 with isomer shifts at δ_1 = 0.29–0.33 mm s^{-1} and δ_2 = 0.33–0.35 mm s^{-1}, respectively. These isomer shifts are lower than expected for a high spin Fe^{3+} state and can be explained by the relatively low coordination number ($n < 6$). The corresponding quadrupole splittings are Δ_1 = 0.23–0.33 mm s^{-1} and Δ_2 = 1.2–1.3 mm s^{-1}, respectively. The latter is rather uncommon for Fe^{3+}, and indicates a strongly perturbed, non-spherical electron density distribution around the iron nucleus. The Mössbauer parameters of the third component, the singlet at δ_3 = 0.54–0.58 mm s^{-1}, correspond well to un-dissolved $FeCl_3$. This was confirmed by performing the measurement at room temperature when the liquid fraction cannot give a spectrum due to a zero Mössbauer–Lamb factor. Indeed, the spectrum showed a singlet with the Mössbauer parameters of $FeCl_3$.[19a] Finally, when a 1.5 fold excess of [bmim]Cl was used, the singlet for $FeCl_3$ was not observed.

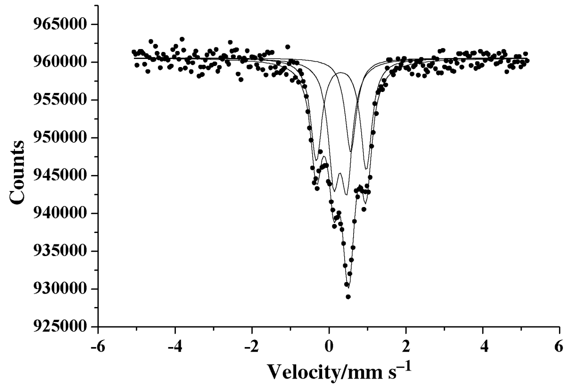


Fig. 5 The Mössbauer spectrum of the frozen ionic liquid prepared from 19 mmol [bmim]Cl and 37 mmol $FeCl_3$ at 80 K (sample **A**).

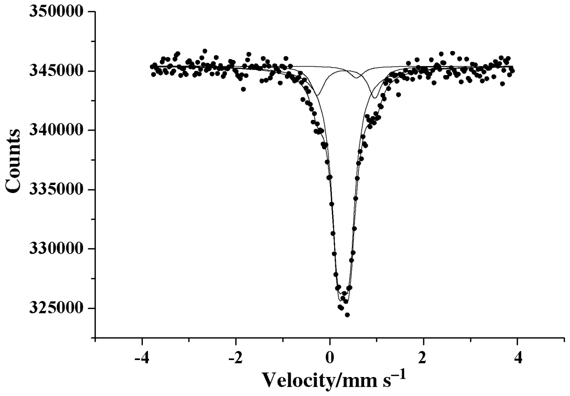


Fig. 6 The Mössbauer spectrum of the frozen ionic liquid prepared from 21 mmol [bmim]Cl and 21 mmol $FeCl_3$ at 80 K (sample **B**).

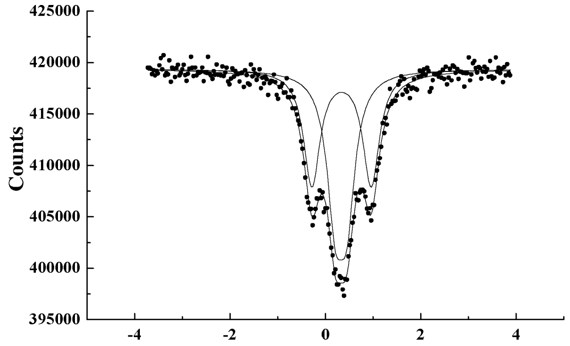


Fig. 7 The Mössbauer spectrum of the frozen ionic liquid prepared from 27 mmol [bmim]Cl and 18 mmol $FeCl_3$ at 80 K (sample **C**).

All three samples contain the binuclear complex [bmim]-$[Fe_2Cl_7]$. In this complex, the four-coordinated iron atom has a distorted tetrahedral ligand sphere resulting in small quadruple splitting, so this can be assigned to doublet 1. The five-coordinated iron atom has a more distorted ligand sphere and is therefore assigned to doublet 2. It should be noted that

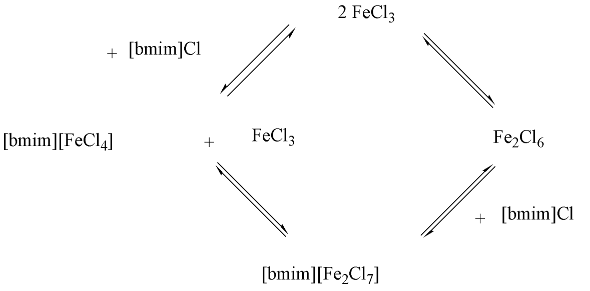
Table 2 The total, relative energies and selected geometry parameters of the computed transition structures

Reaction pathway	Adduct-1	Adduct-2	Ionic
Total energy[a]/hartree	−2468.9131075	−2468.9261545	−2468.9413502
Relative energy[b]/kcal mol^{-1}	17.72	9.54	0.00
r_{CH}[c]/Å	1.172	1.322	1.130
r_{CC}[c]/Å	1.570	1.566	1.659
α_{CCC}[c]/°	158.54	165.41	131.05

[a] The transition structures were optimized at the B3LYP/6-31G(d′,p′) level of theory. [b] The relative energies are the differences from the lower energy TS found. [c] Scheme 4.

Ginsberg and Robin[19b] measured the Mössbauer spectra of two polymorphs of $Cs_3Fe_2Cl_9$ but observed much larger isomer shifts and small or zero quadrupole splittings. To the best of our knowledge, no other Mössbauer studies on polynuclear chloro complexes of iron have been reported. When the molar ratio of [bmim]Cl and $FeCl_3$ was changed from 1 : 2 (sample **A**) to 1 : 1 (sample **B**), the concentration of solid $FeCl_3$ and [bmim][Fe_2Cl_7] decreased and a new species formed. This species has a doublet at exactly the position of doublet 1 and contains either one or more four-coordinated iron atoms. We propose that this species could be either Fe_2Cl_6 and/or [bmim][$FeCl_4$].[19c] Finally, when the molar ratio of [bmim]Cl and $FeCl_3$ was changed to 1.5 : 1 (sample **C**) the dominant species is [bmim][Fe_2Cl_7] and only a small amount of Fe_2Cl_6 and/or [bmim][$FeCl_4$] is present.

We propose that the addition of $FeCl_3$ to [bmim]Cl leads to an equilibrium mixture containing solid $FeCl_3$, [bmim][Fe_2Cl_7], and Fe_2Cl_6 or [bmim][$FeCl_4$] depending on the molar ratio of [bmim]Cl and $FeCl_3$ (Scheme 3).



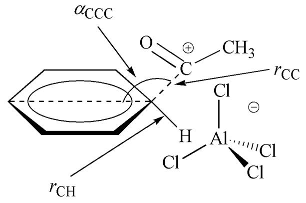
Scheme 3

The mechanism of the Friedel–Crafts acetylation of benzene with acetyl chloride in the presence of MCl_3 (M = Al or Fe)

Concerning the overall reaction mechanism, our results combined with our previous findings[14] indicate that the reaction starts with the activation of the acetyl chloride by the Lewis acids MCl_3 (M = Al or Fe) to form various adducts of acetyl chloride with MCl_3 (Scheme 1). These complexes are in rapid equilibrium with the acetylium ion $[CH_3CO]^+[MCl_4]^-$. There are several mechanistic possibilities for the formation of the C–C bond leading to the MCl_3 adduct of acetophenone, the final product of the reaction, and HCl.

Although the most accepted mechanism involves the acylium ion $[CH_3CO]^+[MCl_4]^-$ as the key intermediate, a direct formation of the MCl_3 adduct of acetophenone from benzene and the $AlCl_3$ adduct of acetyl chloride is also conceivable. Since the experiments did not provide unambiguous proof or disclaimer, exploratory computations were carried out to investigate the possible reaction pathways (Table 2). The description of the geometry parameters can be found in Scheme 4.

The direct reaction path goes through σ-bond metathesis, by breaking and forming four bonds, arranged as a four-membered ring, simultaneously. In this scenario, the chlorine atom of the acetyl chloride assists in releasing the proton from the benzene ring while the C–C bond of the acetophenone adduct forms in a single step. An earlier study[20] found that the



Scheme 4 Description of geometry parameters in Table 2.

$CH_3ClO{\longrightarrow}AlCl_3$ adduct is the most stable form, which also supported our assumptions. The computed structure of the corresponding transition state (TS) is shown in Fig. 8a. The existence of the TS, however, does not necessarily mean that it belongs to a thermodynamically or kinetically favored reaction path, therefore, we continued searching towards other possible pathways for comparison purposes. The same reactants can also approach proper TS from a different orientation, *e.g.* rotating around the forming C–C bond (Fig. 8b). Due to the different orientation the acetyl chloride's chlorine atom appears at the other side of the benzene ring allowing the $AlCl_3$ to participate in the reaction. Three of the bonds involved in the reaction are placed in a six-membered ring-like structure, which provides more flexibility than the four-membered ring of the previously discussed TS. The latter is also energetically favorable, as it is lower in energy by more than 8 kcal mol^{-1} (Table 2). For the sake of completeness we tried to find the TS corresponding to the generally accepted ionic pathway, where the acetylium ion and benzene reacts with the assistance of the $AlCl_4^-$ anion (Fig. 9). In that case, the TS appears earlier during the course of the ionic reaction, since the acetylium ion can more readily accept electrons without the necessity of relaxing an existing bond. The TS for the ionic mechanism gains an extra, almost 10 kcal mol^{-1} advantage, making it the most favorable reaction pathway, if the acetylium cation is present in the solution. The

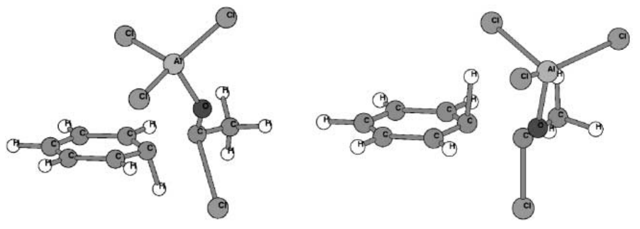


Fig. 8 The transition structures for the Friedel–Crafts reaction of $CH_3ClO{\longrightarrow}AlCl_3$ with benzene.

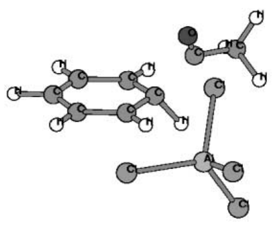


Fig. 9 Transition structure for the Friedel–Crafts acetylation.

non-ionic mechanisms, however, should also be considered as alternatives in environments where the formation of the ion pairs is limited.

Conclusions

We have established that the ionic liquids prepared from [bmim]Cl and either $AlCl_3$ or $FeCl_3$ contain structurally similar species such as MCl_3, [bmim][M_2Cl_7], and M_2Cl_6 and/or [bmim][MCl_4]. The relative ratio between these species depends on the molar ratio of [bmim]Cl and MCl_3. We have also confirmed that the acetylium cation $[CH_3CO]^+[MCl_4]^-$ (M = Al or Fe) is the key intermediate in the Friedel–Crafts acetylation reactions of benzene in these ionic liquids. We have shown that the formation of $[(CH_3CO)_2CHCO]^+[MCl_4]^-$ involves the reaction of the acetylium cation with free acetyl chloride. In general, the formation of $[(CH_3CO)_2CHCO]^+$-$[MCl_4]^-$ could lower the atom economy of the acetylation of aromatics and can be avoided by keeping the concentration of the acetyl chloride below one equivalent with respect to the Lewis acid.

Experimental

General

Acetyl chloride, $AlCl_3$ (99.99%), 1-chlorobutane, and 1-methylimidazole were obtained from Aldrich Chemical Co. and were used as received. Acetic anhydride and benzene were obtained from Reanal, iron(III) chloride (98%) from Merck. The halogenated solvents were distilled from CaH_2 under a N_2 atmosphere before use. All operations were performed under a N_2 atmosphere using a glove box or a dry bag (Aldrich Chemical Co.). All *in situ* infrared spectroscopic experiments were performed using the ReactIR 1000 spectrometer (Applied Systems Inc., a Mettler-Toledo Company: www.asirxn.com). A conventional constant acceleration type Mössbauer spectrometer was used (Ranger) with a ^{57}Co(Rh) source of 400 MBq activity.

The theoretical computations were carried out in the framework of the Gaussian 98[21] quantum chemical program package at the B3LYP/6-31G(d′,p′) level of theory and the GDIIS (geometry optimization using direct inversion in the iterative subspace) based optimization algorithm.[22] The presented transition structures were validated by analytical force constant calculations. The optimized structures are available as Gaussian input at http://organ.elte.hu/farkas/suppl.mat

Preparation of 1-butyl-3-methylimidazolium chloride, $[bmim]^+Cl^-$

The ionic liquid 1-butyl-3-methylimidazolium chloride was prepared by the method of K. Seddon (The Queen's University of Belfast, Northern Ireland): a 100 ml three necked round-bottomed flask was charged with 1-methylimidazole (22 ml, 276 mmol, freshly distilled from CaH_2) and 1-chlorobutane (33 ml, 287 mmol) and heated to 75 °C for 48 hours under N_2. The excess of 1-chlorobutane was removed *in vacuo* at 80 °C. The pale yellow ionic liquid solidifies at room temperature forming a pale yellow solid (99% isolated yield).

Preparation of 1-butyl-3-methylimidazolium heptachlorodialuminate, $[bmim]^+[Al_2Cl_7]^-$

1-Butyl-3-methylimidazolium chloride (17.5 g, 100 mmol) was mixed with $AlCl_3$ (13.3 g, 100 mmol) in a 50 ml three necked round-bottomed flask under N_2 for 5 minutes resulting in a pale yellow liquid (30.8 g, 100% isolated yield).

Preparation of $FeCl_3$ containing ionic liquid

1-Butyl-3-methylimidazolium chloride (17.5 g, 100 mmol) was mixed with $FeCl_3$ (16.2 g, 100 mmol) in a 50 ml three necked round-bottomed flask under N_2 for 5 minutes resulting in a black liquid (33.7 g, 100% isolated yield).

Preparation of samples for Mössbauer measurements

The Mössbauer spectra were recorded at liquid nitrogen temperature. A few droplets of the sample were sealed in a small polyethylene bag of 1 cm^2 so that the liquid formed a thin film inside. This small sample was then dropped into liquid nitrogen to provide fast cooling in order to preserve the chemical equilibrium at room temperature. The frozen sample was placed into the pre-cooled cryostat to record the Mössbauer spectrum. All isomer shifts are given relative to α-Fe at room temperature.

Reaction of acetyl chloride with MCl_3 (M = Al, Fe) containing ionic liquids

A 100 ml three necked round-bottomed flask fitted with gas inlet tube, Suba-seal, and the IR probe of the ReactIR 1000 instrument was charged with the appropriate amount of MCl_3 (M = Al, Fe) containing ionic liquid under N_2. After collecting the first IR spectrum the calculated amount of acetyl chloride was injected using a syringe and the reaction was continuously monitored by IR at room temperature.

Friedel–Crafts acetylation of benzene with acetyl chloride in MCl_3 (M = Al, Fe) containing ionic liquids

A 100 ml three necked round-bottomed flask fitted with gas inlet tube, Suba-seal, and the IR probe of the ReactIR 1000 instrument was charged with the appropriate amount of MCl_3 (M = Al, Fe) containing ionic liquid under N_2. After collecting the first IR spectrum the calculated amount of acetyl chloride was injected using a syringe and the reaction was continuously monitored by IR at room temperature. After a few hours benzene was added to the reaction mixture and the reaction monitoring was continued.

Acknowledgements

This work was partially supported by the Hungarian National Scientific Research Fund (OTKA T-032850 and D-29446) and ExxonMobil Research and Engineering Company, Annandale, New Jersey, USA. The donation of the ReactIR 1000 instrument by Applied Systems Inc, a Mettler-Toledo Company is greatly appreciated. We thank Prof. András Perczel and the Eötvös Univeristy's Compaq High Performance Computing Center for providing CPU time. Ö. F. thanks the Hungarian Academy of Sciences for a János Bolyai Research Scholarship. We also thank Prof. K. Seddon and Dr J. Holbrey, The Queen's University of Belfast, Northern Ireland, for providing the synthetic procedure for 1-butyl-3-methylimidazolium chloride.

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