In situ IR and NMR spectroscopic investigation of the formation and structure of protonated diacetylketene tetrachloroaluminate

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In situ IR and multinuclear NMR are used to monitor the formation of protonated diacetylketene tetrachloro-aluminate (**1**) in the reaction of acetyl chloride and AlCl₃ in both dichloromethane and in 1-butyl-3-methyl-imidazolium chloride ([bmim]Cl). The existence of a fast equilibrium between two enolic forms of protonated diacetylketene (with [AlCl₄]⁻ as the counterion) is established. The structure of **1** is determined by the rarely used ¹³C{¹H}–¹³C{¹H} COSY experiment.

Introduction

The application of stoichiometric amounts of reagents in chemical manufacture always leads to the formation of spent reagents, which have to be either regenerated or discharged as waste, frequently resulting in serious environmental problems.[1] Waste minimization can be achieved by the replacement of a reagent with a catalyst provided the catalytic reaction is atom efficient.[2] Since the formation of side-products could decrease the atom economy of a catalytic approach, their characterization and the determination of the mechanism involved is crucial for the development of waste-free green processes.

The Friedel–Crafts acylation is one of the basic reactions in organic chemistry.[3] Although several investigations have been performed to establish the exact reaction mechanism,[3,4] the characterization of all reaction intermediates and side-products is still not complete. It is well established that the initial step is the interaction of the acyl halide with the Lewis acid leading to different donor–acceptor complexes followed by the facile formation of the acylium ion (RCO⁺).[5,6] It should be noted that in the case of acetylation with CH_3COCl in the presence of $AlCl_3$, the formation of a side product, the diacetylacetylium tetrachloroaluminate, $[(CH_3CO)_2CHCO]^+[AlCl_4]^-$ (**1**), was observed by IR and ¹H-NMR.[3c,7] It has been proposed that this compound has two different tautomer forms (Scheme 1, structures **1a**–**1d**) and it forms *via* the trimerization of the acylium ion $[CH_3CO]^+[AlCl_4]^-$. In addition, the formation of polymeric species has also been noted. In the contrary, the reaction of CH_3COCl with $AlCl_3$ at a molar ratio of 1:1 in CD_2Cl_2 does not lead to **1** and only the formation of the donor–acceptor complexes of CH_3COCl and $AlCl_3$, and acetylium ion were observed.[8]

The analogous $[(CH_3CO)_2CHCO]^+[SbF_6]^-$, called the diaceto-acetylium hexafluoroantimonate, was isolated and the existence of a fast equilibrium between two enolic forms was established by IR and NMR.[9] Since the presence of a methyne carbon could not be established using ¹H-coupled ¹³C-NMR, a significant contribution of a "ketene-like" resonance form was suggested (Scheme 1, structures **1b** and **1c**). Consequently, we believe that the compound is best described as protonated diacetylketene hexafluoroantimonate with two enolic forms. Although the same structures were proposed for the tetra-chloroaluminate salt as well, no supporting spectroscopic evidence was provided.
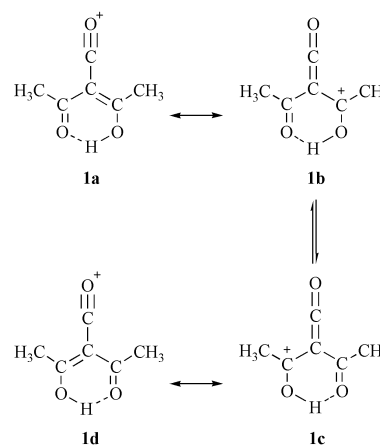
Scheme 1

We have recently shown by *in situ* IR that the acetylation of benzene in the presence of MCl_3 (M = Al, Fe) in both 1,2-dichloroethane and in ionic liquids proceeds through the same mechanism.[10,11] The slow formation of **1** was noted and it was shown that it requires the presence of acetyl chloride in excess with respect to $AlCl_3$.[11] We report here the results of a detailed *in situ* NMR investigation on the formation of **1** including its complete structural characterization.

Results and discussion

We have investigated the reaction of CH_3COCl and 99% ¹³C-labelled $CH_3{}^{13}COCl$ with $AlCl_3$ in CD_2Cl_2 by IR. In the case of CH_3COCl, the position and the time-profile of the peaks (Fig. 1) are the same as in 1,2-dichloroethane.[10,11] The band at 1800 cm⁻¹ (A) is due to acetyl chloride and the bands at 1644 (B) and 1571 (C) cm⁻¹ are assigned to the 1:1 and 1:2 complexes of acetyl chloride and $AlCl_3$, respectively. The bands of **1** appear at 2200 (D) and 1636 (E) cm⁻¹. When the reaction is repeated with $CH_3{}^{13}COCl$, all the bands are shifted to lower wave numbers, as expected. Thus, the band of $CH_3{}^{13}COCl$ appears at 1760 cm⁻¹ (A′), while the bands of the 1:1 and 1:2 complexes are shifted to 1617 (B′) and 1525 (C′) cm⁻¹, respectively. Finally, the bands of **1** are at 2138 (D′) and 1594 (E′) cm⁻¹. In addition, the time-profiles of these peaks are the same as for CH_3COCl.

Table 1 Chemical shift and coupling constant values

Species	^{1}H-NMR		^{13}C-NMR					
	δ/ppm	LW/Hz	δ/ppm	LW/Hz	$^1J_{CC}$/Hz	$^2J_{CC}$/Hz	$^1J_{CH}$/Hz	$^2J_{CH}$/Hz
CH$_3$COCl	2.70	1.3	170.7	1.8	56.4	—	132.9	7.4
			33.9	1.3				
Donor–acceptor complexes[a]	2.83	1.6	178.5	11.4	54.5	—	133.3	7.2
			34.7	6.6				
1 in CD$_2$Cl$_2$	—[b]	—	207.1–207.9[b]	—	—	—	—	—
			169.3–170.1					
			77.5–79.2					
			31.8–32.7					
1 in ionic liquid	2.33	1.2	207.3	1.8	45.8; 59.6	6.4	133.3	7.6
			169.7	1.8	98.0	2.8; 3.3		
			78.0	1.8	98.0; 59.6	8.25		
			31.5	1.8	45.8	3.7; 4.6		

[a] Donor–acceptor complexes of CH$_3$COCl and AlCl$_3$. [b] Too small intensity, negligible peaks, the region in which they appear is given.
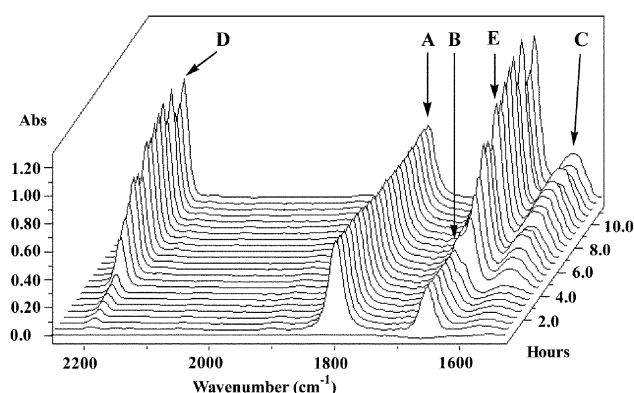

Fig. 1 *In situ* IR spectra of the reaction of AlCl$_3$ and CH$_3$COCl in CD$_2$Cl$_2$.

The application of ^{13}C-NMR for the characterization of **1**, prepared from 99% ^{13}C-labeled CH$_3$^{13}COCl, was limited as the intensities of the peaks due to the non-labelled carbons were negligible. Therefore, the *in situ* NMR investigation was repeated using 99% ^{13}C-labelled ^{13}CH$_3$^{13}COCl.

First, the ^{1}H- and ^{13}C-NMR of ^{13}CH$_3$^{13}COCl in CD$_2$Cl$_2$ was recorded. While the ^{1}H-NMR exhibits a doublet of doublets due to the coupling of the two C atoms, by one and two bonds, respectively, the ^{13}C{^{1}H} spectrum consists of two doublets with the same coupling constant, as shown in Table 1. Then, solid AlCl$_3$ was added under N$_2$ resulting in the final solution containing 7.5 mmol ^{13}CH$_3$^{13}COCl and 1.5 mmol AlCl$_3$ (ratio 5:1) in 10 mmol CD$_2$Cl$_2$.

In the ^{1}H- and ^{13}C-NMR spectra recorded immediately after the dissolution of the solid AlCl$_3$ the chemical shifts of the methyl groups, and the coupling constant values, do not change significantly. In contrast, there is an 8 ppm change in the chemical shift of the carbonyl groups. It should be noted that the IR has showed separate carbonyl vibrations for the free acetyl chloride and for the various donor–acceptor complexes of CH$_3$COCl and AlCl$_3$. It appears that the exchange between the free and coordinated acetyl chloride is so fast on the NMR time scale, that only the averaged signal could be observed at room temperature. The 11.4 Hz line width of this signal compared to the 1.8 Hz value for the free CH$_3$COCl also confirms the existence of this exchange. The time dependent ^{13}C{^{1}H} spectra show the appearance of new peaks at around 207, 170, 78 and 32 ppm, as shown in Fig. 2 (see also Table 1). On the basis of

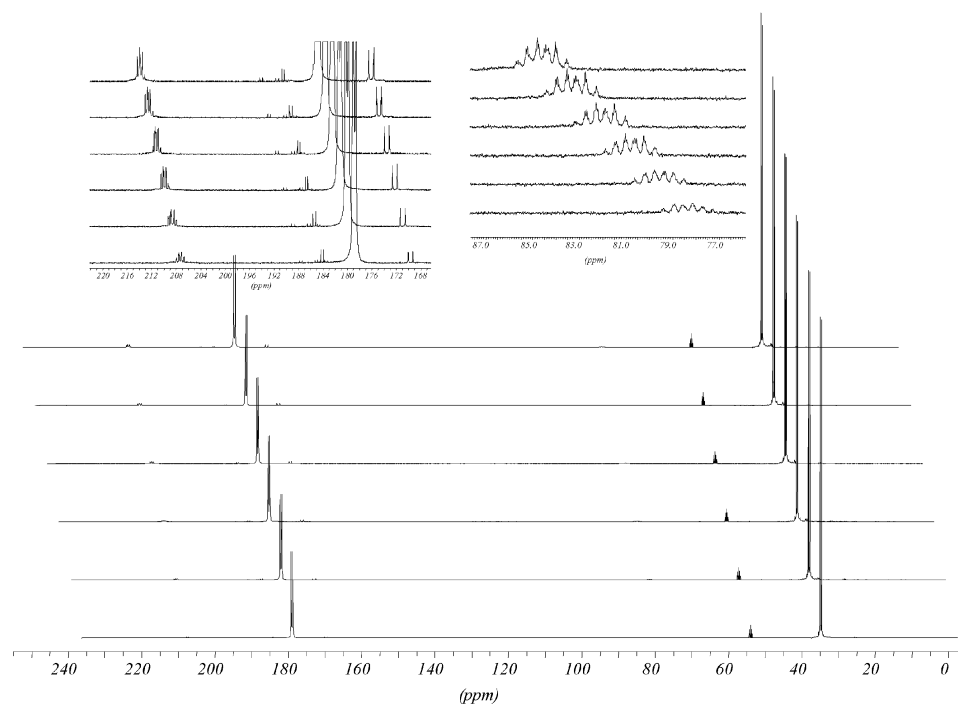**Fig. 2** ^{13}C{^{1}H}-NMR spectra recorded at 3, 7, 9, 12, 15, 17 hours (beginning from the bottom spectrum) after mixing a solution containing 7.5 mmol ^{13}CH$_3$^{13}COCl and 1.5 mmol AlCl$_3$ in CD$_2$Cl$_2$. The two zoomed figures belong to the new signals.

previous IR and NMR results the appearance of these peaks is consistent with the formation of **1**. However, their intensity is very low compared to those of the acetyl chloride signals and there is no dramatic change in their intensities during the next 18 hours. It should be noted, that the solubility of **1** is limited in CD_2Cl_2 and the formation of a second colourless glassy-phase was observed at the bottom of the tube.

Since the solubility of **1** in ionic liquids is expected to be higher, we have repeated the reaction in [bmim][Al_2Cl_7]. The ratio of 5:1 between the acetyl chloride and $AlCl_3$ is achieved by adding 3.35 mmol acetyl chloride (1.82 mmol $^{13}CH_3{}^{13}COCl$ and 1.53 mmol CH_3COCl) to 0.34 mmol [bmim][Al_2Cl_7] (equivalent to 0.67 mmol $AlCl_3$) in an NMR tube under N_2. ^{1}H-NMR spectra taken immediately after mixing show a broad multiplet due to the methyl groups of several species including donor–acceptor complexes of CH_3COCl and $AlCl_3$ (see Fig. 3). The
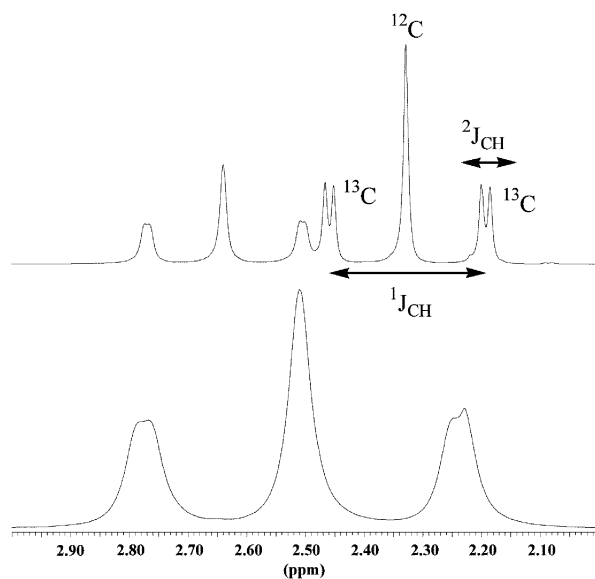

Fig. 4 Time evolution (from bottom at 1, 1.5, 3, 4, 6, 8, 10, 12, 14 hours after mixing) of the $^{13}C\{^1H\}$-NMR carbonyl region at 125 MHz of a sample containing 0.34 mmol [bmim][Al_2Cl_7] and 3.35 mmol acetyl chloride (1.82 mmol $^{13}CH_3{}^{13}COCl$ and 1.53 mmol CH_3COCl). The small peaks at 184, 168 ppm are due to the ionic liquid.

Fig. 3 ^{1}H-NMR spectra recorded after mixing (bottom spectrum) and after one day (top spectrum) of a sample containing 0.34 mmol [bmim][Al_2Cl_7] and 3.35 mmol acetyl chloride (1.82 mmol $^{13}CH_3{}^{13}COCl$ and 1.3 mmol CH_3COCl).

Fig. 5 ^{13}C–^{13}C proton decoupled COSY spectra at 125 MHz for a sample containing 0.34 mmol [bmim][Al_2Cl_7] and 3.35 mmol acetyl chloride (1.82 mmol $^{13}CH_3{}^{13}COCl$ and 1.53 mmol CH_3COCl).

structure of the broad multiplet originates from the fact that both labelled and non-labelled carbons are present. The labelled ones give rise to a doublet of doublets, while the non-labelled is a singlet. After one day, the intensities of the originally broad methyl signals decrease and a downfield shift in their position is observed, *i.e.* the central peak is shifted from 2.51 ppm to 2.64 ppm. At the same time a new set of sharp resonances appeared at 2.33 ppm.

The progress of the reaction was monitored by ^{13}C-NMR. While all NMR data are reported in Table 1, the change in the carbonyl region is shown in Fig. 4. At the beginning of the reaction broad signals are observed at 176.4 and 33.0 ppm indicating the presence of various donor–acceptor complexes of CH_3COCl and $AlCl_3$, in accordance with the ^{1}H-NMR results. These broad signals have continuously shifted to 172.4 ppm and 34.3 ppm, respectively, in the next 14 hours and become well-resolved but still broad doublets, as expected. In the same time several new resonances have appeared at 207.3, 169.7, 78.0, and 31.5 ppm and their relative integrals are 2:1:1:2. These resonances are assigned to **1**. While the peaks at 207.3 and 169.7 are due to the carbonyl groups, the resonance at 31.5 ppm is assigned to the methyl groups. Since the peak at 78.0 ppm does not appear in the ^{13}C-NMR spectra recorded with DEPT135 pulse sequence, it can only be assigned to a carbon atom without directly attached proton(s). The connectivity between these peaks can be established by ^{13}C–^{13}C COSY correlation, which is shown in Fig. 5 (resonances due to **1** are marked with asterisks
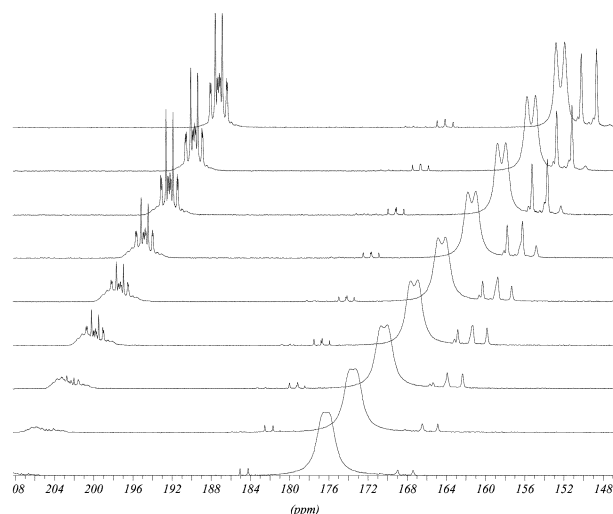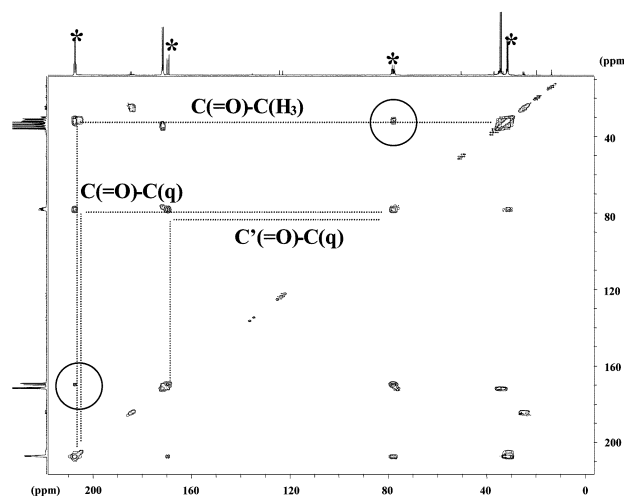
(*) on the top 1D spectrum). COSY cross peaks appear between neighbouring carbon signals and the straight lines help the assignment of the direct C–C bonds, while the less intensive cross peaks, visualized by circles, are two-bond distanced carbons. While the established connectivities are consistent with structures **1a**–**1d** on Scheme 1, the observed coupling constants (Fig. 6) provide further structural information. Thus, literature
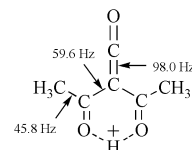

Fig. 6 One-bond carbon–carbon coupling constant values of **1**.

data of one-bond carbon–carbon spin–spin coupling constant values for (i) a simple bond with two sp^3 hybridized carbons (CH_3–CH_3) is 34.6 Hz, (ii) simple bond with one sp^3 and one sp hybridized carbon (CH_3–$C{\equiv}CH$) is 67.4 Hz, (iii) double bond with two sp^2 hybridized carbons ($CH_2{=}CH_2$) is 67.2 Hz, and (iv) double bond with unusual hybridization as for allenes ($CH_2{=}C{=}CH_2$) is 98.7 Hz.[12] Therefore, our measured value of

98.0 Hz supports the "ketene-like" structures **1b,c** (Scheme 1). In addition, the most intensive signal at 104.8 ppm, observed by ^{27}Al-NMR, confirms the presence of the [AlCl$_4$]$^-$ counter anion in **1**, as expected.

Since both labelled and non-labelled carbons are present in the sample, the coupling pattern of the signals can be predicted from the structure proposed for **1b,c**. Indeed, the predicted pattern of the resonance at 78.0 ppm is observed experimentally (Fig. 7).
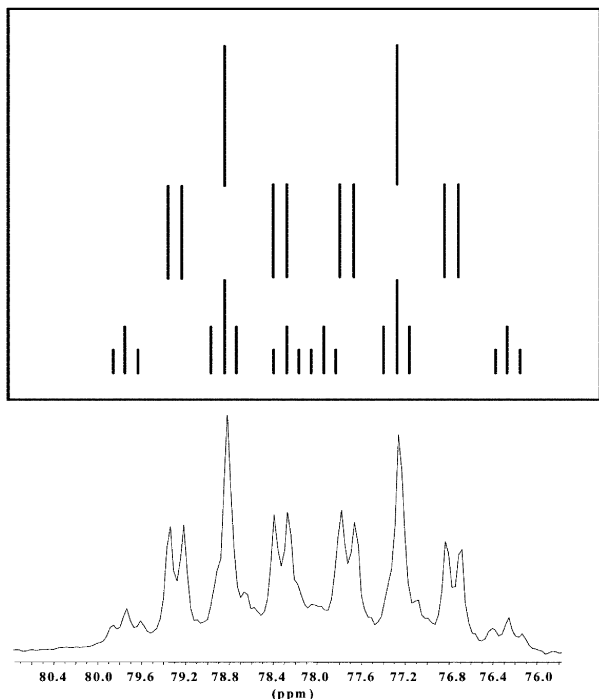

Fig. 7 The splitting in the ^{13}C-NMR spectrum of the carbon atom at 78.0 ppm.

Finally, it should be emphasized that protonated diacetyl-ketene (with [AlCl$_4$]$^-$ as the counter anion) is best described as a pair of enolic structures that are in rapid equilibrium and wherein each enolic structure may be described by a number of contributing resonance structures.

Experimental

General

Acetyl chloride and AlCl$_3$ (99.99%) were obtained from Aldrich Chemical Co. and were used as received. Acetyl chloride (1,2-13C2, 99%) and methylene chloride-d$_2$ (D, 99.9%) were purchased from Cambridge Isotope Laboratories, Inc. The ionic liquid was prepared by a known method.[11] All operations were performed under N$_2$ atmosphere. All *in situ* infrared spectroscopic experiments were performed in standard glassware under N$_2$ using the ReactIR 1000 spectrometer (Applied Systems Inc, a Mettler-Toledo Company: www.asirxn.com). NMR measurements were performed on Bruker 250 and 500 MHz instruments. An inverse gated decoupling sequence was used for quantitative carbon measurements. A home-made ^{13}C–^{13}C COSY with ^{1}H decoupling sequence was used for ^{13}C-labelled samples. All measurements were performed at 25 °C.

In situ IR measurement of the reaction of acetyl chloride with AlCl$_3$ in CD$_2$Cl$_2$

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 AlCl$_3$ (40 mg, 0.3 mmol) and

CD$_2$Cl$_2$ (1.0 ml, 15.7 mmol) under N$_2$. CH$_3$^{13}COCl (0.1 ml, 1.5 mmol) was injected using a syringe and the reaction was continuously monitored by IR.

In situ NMR measurement of the reaction of acetyl chloride with AlCl$_3$ in CD$_2$Cl$_2$

^{13}CH$_3$^{13}COCl (0.1 ml, 1.5 mmol) and CD$_2$Cl$_2$ (1.0 ml, 15.7 mmol) was charged into an NMR tube under N$_2$. After recording ^{1}H- and ^{13}C-NMR spectra solid AlCl$_3$ (40 mg, 0.3 mmol) was added to the solution and the reaction was monitored by ^{1}H- and ^{13}C-, ^{27}Al-NMR.

In situ NMR measurement of the reaction of acetyl chloride with AlCl$_3$ in [bmim]Cl

3.35 mmol acetyl chloride (a mixture of 1.82 mmol ^{13}CH$_3$^{13}COCl and 1.53 mmol CH$_3$COCl) was added to [bmim]-[Al$_2$Cl$_7$] (296 mg, 0.34 mmol) in an NMR tube under N$_2$. The reaction was monitored by ^{1}H- and ^{13}C-, ^{27}Al-NMR.

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