Application of low temperature IR spectroscopy for studies of catalyst properties and dynamics on the example of aluminum halide complexes

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Abstract

This paper shows the benefits of applying IR spectroscopy to solid state studies of active labile catalytic complexes, intermediates and reaction mechanisms taking aluminum halide complexes as an example. Aluminum halide complexes with ethylene, hydrogen chloride and organic nitrocompounds were prepared under codeposition of reagents on a cooled surface and then films obtained were studied at 80–150 K. Semi-empirical and ab initio calculations were used to analyze spectral data. A limited molecular mobility and special features of the solid state make it possible to investigate the nature and properties of different types of complexes. In addition, direct observation of catalytic species unstable in solutions becomes possible. Structure and reactivity of a number of molecular and ionic monomer and dimer aluminum halide complexes were studied. Dimer complexes are more active and may catalyze hydrohalogenation of ethylene and dehydration of nitrocompounds even at low temperatures. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aluminum halide; Complex; Structure; Catalysis; Mechanism; IR spectroscopy; Solid state; Low temperature

1. Introduction

The background to this work lies in the unique chemical properties of superacids based on metal halides. These are known to be associated in the condensed state and have been found to act as very effective catalysts for a number of important organic reactions, such as alkane activation, Friedel–Crafts alkylation, isomerization, hydrohalogenation and halogenation [1–5]. Catalytic properties of aluminum halide associates taken as an example of strong Lewis acid are manifested clearly at low temperatures in solid state [6]. The reactivity of aluminum chloride complexes is so high that even at low temperatures (ca. 100 K) their catalytic effect may be observed at a rate which can be followed by infrared spectroscopic monitoring. The interaction of two or more metal halide molecules causes a dramatic increase in both catalytic activity and Lewis acidity. At the present time, there is little data on the nature of the active intermediates formed in strong Lewis acids. The reasons for unusually high reactivity of polynuclear metal halide complexes and key stages of catalytic reactions are not clear in spite of a number of investigations devoted to this problem. The investigation of such catalytic system under usual conditions (solution, room temperature) is a difficult problem in view of rapid

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equilibria between several complexes with different activity. These equilibria are frozen out in the solid state and the nature and properties of different types of complexes can be investigated. In addition, direct observation of catalytic species unstable in solutions becomes possible because of a limited molecular mobility and special features of the solid state.

Low temperature IR spectroscopy can be used in the solid state to study catalyst complexes with reagents, catalytic intermediates, their dynamics and reaction mechanisms. The benefits of applying this method to intermediate complexes and reaction mechanism studies have been shown in molecular halogenation investigation [7,8]. This work demonstrates the possibilities of this technique taking aluminum halide complexes as an example of high active catalysts.

Two systems were investigated: aluminum halide–hydrogen chloride–ethylene and aluminum halide–nitroalkane. Ethylene hydrochlorination in the presence of aluminum halide is an example of one of a few catalytic processes occurring in both liquid and solid phases at low temperatures, 100–180 K. The second reaction order with respect to aluminum halide in solution [9] may be considered as an indication of participation of polynuclear complexes in catalysis. Aluminum chloride is the most frequently used as a catalyst in nitroalkane solution, for example, in Ref. [10]. Polynuclear species may also play an important role in catalysis in this solution. Aluminum chloride complexes with nitroalkanes of different than 1:1 composition have not been studied formerly.

2. Experimental

Aluminum halides (99.99%) were purified by sublimation and stored in sealed ampules. The purity of reactants was checked with IR spectroscopy by measuring the intensity of the bands in the range of 3200 cm^{-1} that correspond to hydrolysis product. The samples to study by IR

spectroscopy (4000–400 cm^{-1}) were obtained in a vacuum by simultaneous or sequential condensation of reagents from gaseous phase on the cold (80 K) copper surface using a reactor with KBr windows described in details in Ref. [11]. The sublimation temperatures for aluminum bromide and chloride were 313 and 343 K, respectively. Other reactants were supplied from ampules under the temperatures which provided the condensation rate in a molecular beam regime [6–8]. It allowed us to ignore the interaction of reactants in the gas phase. The average preparation time of the samples was between 30 and 60 min, the film thickness did not exceed 3–5 μm. After reactant condensation the reactor was disconnected from the vacuum apparatus and placed in Specord 75-IR spectrometer.

Depending on condensation conditions (temperature, rate of condensation, reagent ratio and sequence of codeposition, inert matrix), samples of a various composition with different spectroscopic characteristics were prepared. The analysis of experimental and theoretical data using semi-empirical and ab initio calculations allowed to associate spectra with the nature of species formed. For example, aluminum halide as a monomer, dimer, crystal, monomer complex or dimer complex was prepared and then the chemical behavior of these forms was studied. The slow transformations of less stable forms to more stable ones and catalytic reactions were observed in systems investigated on warming up to 150 K.

Chromatographic analysis of the reaction products was performed on Chrom-5 chromatograf after warming of the samples.

3. Results and discussion

3.1. Aluminum halide–hydrogen chloride–ethylene system

Different spectroscopic characteristics and chemical properties were found for samples obtained under various sequence of aluminum

halide codeposition with ethylene and hydrogen chloride. The spectra observed in solid films have been discussed in detail previously in Ref. [6]. The frequencies of the main absorption bands in IR spectra of solid cocondensates obtained under different conditions are summarized in Table 1. As can be seen, monomer aluminum halide complexes and its molecular dimer are formed under binary codeposition with ethylene and hydrogen chloride. When aluminum halide complex with ethylene of 1:1 composition prepared previously was used as an initial state for reaction with hydrogen chloride only ethylene oligomerization catalyzed by aluminum halide and hydrogen chloride was detected at 100 K. In contrast, ethylene hydrochlo-
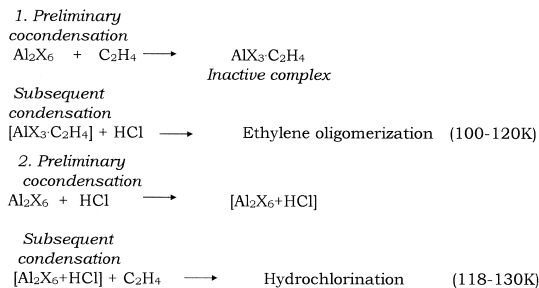
rination proceeded even at 118 K when aluminum halide and hydrogen chloride cocondensates were applied for reaction with ethylene. The formation of aluminum halide monomer or dimer complexes with hydrogen chloride was not detected. The sequence of processes is made clearer by Scheme 1.

The most active catalyst for hydrochlorination was found to be a mixed aluminum halide $Al_2Br_2Cl_4$ prepared by the interaction of aluminum bromide with excess of hydrogen chloride at 118–150 K. The mixed halides are characterized by the new absorption bands in the range of 600–500 cm^{-1} [6]. The catalytic hydrochlorination is likely to proceed via ionic intermediates containing both reagents and two

Table 1
IR spectra of HCl–(Al_2X_6)/AlX_3–C_2H_4 cocondensates and reaction conditions

Species	ν_{Al-X} (cm^{-1})	New bands (cm^{-1})	Product	Conditions
$AlCl_3$	610			
$AlCl_3 \cdot D$	540			C_2H_4, C_2H_5X
$D = C_2H_4$, C_2H_5X				80 K
$AlBr_3$	490			
$AlBr_3 \cdot D$	440			C_2H_4, C_2H_5X, 80 K
$D = C_2H_4$, C_2H_5X				
Al_2Cl_6	606, 465			
$AlCl_3 \cdot C_2H_4$	408			C_2H_4, 80 K
	540	2960, 2880, 1380, 1280	Ethylene oligomers	HCl, 120 K
Al_2Br_6	495			
$AlBr_3 \cdot C_2H_4$	440			C_2H_4, 80 K
		2960, 2880, 1380, 1280	Ethylene oligomers	HCl, 100 K
Al_2Br_6	495			HCl, 80 K
$Al_2Br_4Cl_2$	595, 560, 506	2460	HBr	HCl, 118 K
$Al_2Cl_4Br_2$	595, 506	2460	HBr	HCl, 130 K
	540, 520	1070, 962, 780, 656, 565	C_2H_5Cl	C_2H_4, 118 K
	intermediate		C_2H_5Br	
Al_2Br_6	495	2460	HBr	HCl, C_2H_4
	595, 506	1070, 962, 780, 656, 565	C_2H_5Cl	130 K
	540, 520		C_2H_5Br	
$Al_2Cl_nBr_{7-n}{}^-$	540, 520			C_6H_6, HCl, 115 K
$AlCl_4{}^-$ [12]	495			
$AlBr_4{}^-$	400			
$AlCl_nBr_{4-n}{}^-$	465, 440, 418			
$Al_2Cl_7{}^-$ [13]	560, 530, 430			
$Al_2Br_7{}^-$	445			

THE PROCESSES IN ALUMINIUM HALIDE - ETHYLENE - HYDROGEN CHLORIDE SYSTEM

1. Preliminary cocondensation
Al_2X_6 + C_2H_4 $\longrightarrow$ $AlX_3 \cdot C_2H_4$
Inactive complex

Subsequent condensation
$[AlX_3 \cdot C_2H_4]$ + HCl $\longrightarrow$ Ethylene oligomerization (100-120K)

2. Preliminary cocondensation
Al_2X_6 + HCl $\longrightarrow$ $[Al_2X_6 + HCl]$

Subsequent condensation
$[Al_2X_6 + HCl]$ + C_2H_4 $\longrightarrow$ Hydrochlorination (118-130K)

Scheme 1. The process inaluminum halide–ethylene–hydrogen chloride system. 1. Preliminary cocondensation: $Al_2X_6 + C_2H_4 \rightarrow AlX_3 \cdot C_2H_4$ (inactive complex); Subsequent condensation: $[AlX_3 \cdot C_2H_4] + HCl \rightarrow$ Ethylene oligomerization (100–120 K). 2. Preliminary cocondensation: $Al_2X_6 + HCl \rightarrow [Al_2X_6 + HCl]$; Subsequent condensation: $[Al_2X_6 + HCl] + C_2H_4 \rightarrow$ Hydrochlorination (118–130 K).

or more molecules of mixed aluminum halide in accordance with Scheme 2.

The conclusion about intermediate formation of ionic species was reached from a comparison of bands observed under warming of aluminum halide–hydrogen chloride–ethylene films with data known for ionic complexes [12,13].

These results explain the data obtained for liquid phase hydrochlorination [9]. The second order with respect to aluminum halide is associated with dimer aluminum halide participation in catalysis of hydrochlorination. The ethylene action as an inhibitor of hydrochlorination revealed by high ethylene concentration may be attributable to the inactive monomer complex formation (Scheme 1).
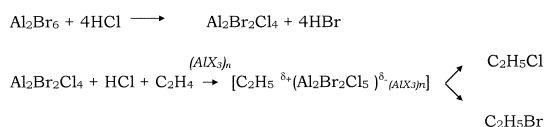
3.2. Aluminum chloride–nitroalkane system

The data obtained for another example of model catalytic system, aluminum chloride–nitroalkane, have shown that a number of molecular and ionic complexes of 1:2, 1:1 and 2:1 compositions with different properties were formed at 80 K, the most active $Al_2Cl_6 \cdot CH_3NO_2$ species catalyzed the nitromethane decomposition even in the solid state at 80–150 K.

The interaction between aluminum halide and nitroalkanes (nitromethane and 1-nitropropane) takes place already at 80 K and gives rise to modifications of their IR spectra. The most shifts are observed in the range of stretch and deformation NO_2-modes and stretch $AlCl_3$ modes (Table 2). As it can be seen from Table 2, the NO_2-asymmetric stretch rose, while the NO_2-symmetric fell under complex formation with aluminum chloride. Moreover the absorption band of the CN-stretch fell. The position and the ratio of the intensities of shifted bands in complexes were dependent on the cocondensate composition and the sequence of condensation. These results can not be interpreted in an assumption of only one complex formation under the observing conditions. The analysis of the observed spectral data performed with consideration for characteristics of reactants and their known 1:1 complexes [15,16] permitted to identify unknown early aluminum chloride–nitroalkane molecular complexes of the 2:1 and 1:2 composition equally to 1:1 one. According to spectral investigation the aluminum chloride–nitromethane complexes of the 1:2 composition exist in solid state only at 80–170 K. Warming to higher temperatures goes over to spectral changes typical for ionic species, jet observed only in solutions.

3.2.1. Quantum chemical calculations

Possible structures of the *aluminum chloride–nitromethane* complexes have been analysed on the basis of semi-empirical PM3 and ab initio methods (for 1:1 and 1:2 complexes). The following species have been found — molecular complexes of $AlCl_3$ monomer of the 1:1, 2:1 and 1:2 composition, molecular Al_2Cl_6 dimer

CATALYTIC HYDROCHLORINATION OF ETHYLENE

Al_2Br_6 + 4HCl $\longrightarrow$ $Al_2Br_2Cl_4$ + 4HBr

$Al_2Br_2Cl_4$ + HCl + C_2H_4 $\xrightarrow{(AlX_3)_n}$ $[C_2H_5 {}^{\delta+}(Al_2Br_2Cl_5){}^{\delta-}]_{(AlX_3)n}$ $\left\{ \begin{array}{l} C_2H_5Cl \\ \\ C_2H_5Br \end{array} \right.$
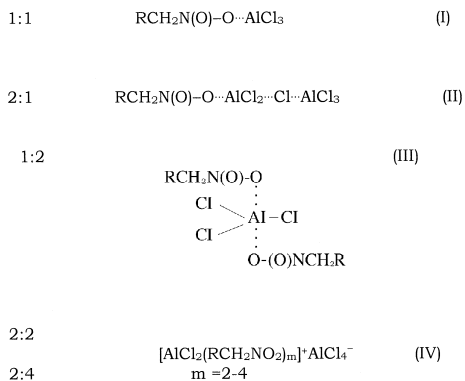
Scheme 2.

Table 2
Experimental (80 K, solid state) and calculated vibrational frequencies of nitromethane, aluminum chloride and their molecular complexes of different composition

Assignment	CH_3NO_2; $AlCl_3$		$AlCl_3 \cdot CH_3NO_2$ (I)		$AlCl_3 \cdot (CH_3NO_2)_2$ (III)		$Al_2Cl_6 \cdot CH_3NO_2$ (II)
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
$\nu(CH_3)$	3073 m	3064 w	3075 m	3070 w	3076 m	3067 w, 3064 w	3072 m
$\nu_a(CH_3)$	3040 w	3025 vw	3035 w	3030 vw	3041 w	3031 w, 3030 w	3038 w
$\nu_s(CH_3)$	2957 w	2937 vw	2950 w	2932 vw	2958 w	2931 w, 2930 w	2956 w
$\nu_a(NO_2)$	1560 vs	1516 vs	1610 s	1648 vs	1608 m	1641 vs	1617 s
	1550 vs				1590 s	1627 vs	1575 w
$\delta(CH_3)$	1435 w	1466 s	1435 vw	1455 w	1435 vw	1463 m, 1459 w	1435 vw
	1420 s	1446 s	1415 m	1449 w	1420 w	1457 w, 1453 w	1414 m
					1415 m		
$\delta(CH_3) + \nu_s(NO_2)$	1378 m	1436 m	1373 m	1426 m	1376 m	1429 m	1373 m
					1373 m	1427 m	
$\nu_s(NO_2) + \nu(CN)$	1403 m	1375 m	1352 m	1334 vs	1356 s	1343 vs	1317 s
			1325 s		1330 m	1334 vs	
$\rho_r(CH_3) + \delta(CNO)$	1120 w	1151 w	1120 w	1151 vw	1120 w	1155, 1154 vw	1120 w
	1105 s	1100 m	1100 s	1115 m	1105 s	1108 w, 1107 w	1105 s
$\nu(CN)$	916 m	890 w	905 m	872 m	916 m	896 w	903 m
					908 w	883 w	
$\delta(NO_2)$	656 s	638 m	673 s	622 s	670 s	633 m	678 s
					660 s	625 w	
$\chi(NO_2)$	605 m	602 w	603 m	589 w	605 m	591 w, 587 w	598 m
$\nu(AlCl)$	618 s[a]	586 s	546 m sh	549 vs	523 s	536 s	563 s
			535 s	543 vs	505 s	479 vs	542 s
							432 w
$\rho_r(NO_2)$	480 w	517 vw	408 vw	567 m	450 vw	507 vw, 505 w	408 vw

[a] for monomer $AlCl_3$ above 400 cm^{-1} in Ar matrix [14].

complexes of the 2:1 composition and, furthermore, ionic structures with the aluminum chloride: nitromethane ratio equal to 2:2 and 2:4 (Scheme 3). The monomer 2:1 and 1:2 complexes are less advantageous. Quantum mechanical calculations of the vibrational frequencies of $AlCl_3$, CH_3NO_2 and their 1:1 and 1:2 complexes were carried out at the STO 6–31 G

level with experimental scale constant $\lambda = 0.9 \pm 0.03$ for the region of vibrational spectrum over 700 cm^{-1} in a similar way to Ref. [17]. The results obtained for following proposed structures are summarized in Table 2 together with experimental data. It can be seen they are in good agreement with the experimental values.
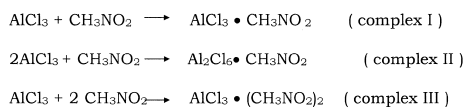
3.2.2. The dynamic of complex transformations in solid system

A limited molecular mobility in a solid state at low temperatures allows to stabilize a number of comparatively labile aluminum chloride complexes with nitroalkanes. The results of the experimental and quantum-chemical research show that aluminum chloride forms with nitroalkane at least four kinds of complex, including unknown earlier polynuclear species with the most Lewis acidity. The following scheme (Scheme 4) shows the possible processes of complex
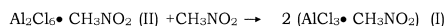
1:1   RCH₂N(O)–O⋯AlCl₃   (I)

2:1   RCH₂N(O)–O⋯AlCl₂⋯Cl⋯AlCl₃   (II)

1:2   (III)

RCH₂N(O)-O
  Cl ⟍
      ⟍ Al – Cl
  Cl ⟋
  O-(O)NCH₂R

2:2   [AlCl₂(RCH₂NO₂)ₘ]⁺AlCl₄⁻   (IV)
2:4   m = 2-4

Scheme 3.

INTERMOLECULAR INTERACTIONS AND TRANSFORMATIONS IN THE
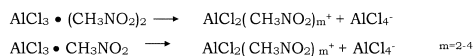ALUMINUM CHLORIDE - NITROMETHANE SYSTEM

Temperature 80 K

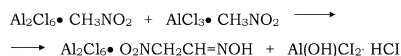$AlCl_3 + CH_3NO_2 \longrightarrow AlCl_3 \bullet CH_3NO_2$ (complex I)

$2AlCl_3 + CH_3NO_2 \longrightarrow Al_2Cl_6 \bullet CH_3NO_2$ (complex II)

$AlCl_3 + 2 CH_3NO_2 \longrightarrow AlCl_3 \bullet (CH_3NO_2)_2$ (complex III)

Temperature 150-230 K

Complex interaction

$Al_2Cl_6 \bullet CH_3NO_2$ (II) $+ CH_3NO_2 \longrightarrow 2 (AlCl_3 \bullet CH_3NO_2)$ (I)

Complex ionization

$AlCl_3 \bullet (CH_3NO_2)_2 \longrightarrow AlCl_2 (CH_3NO_2)_m{}^+ + AlCl_4{}^-$

$AlCl_3 \bullet CH_3NO_2 \longrightarrow AlCl_2 (CH_3NO_2)_m{}^+ + AlCl_4{}^-$ m=2-4

Nitromethane catalytic dehydration

$Al_2Cl_6 \bullet CH_3NO_2 + AlCl_3 \bullet CH_3NO_2 \longrightarrow$

$\longrightarrow Al_2Cl_6 \bullet O_2NCH_2CH=NOH + Al(OH)Cl_2 \bullet HCl$

Scheme 4. Intermolecular interactions and transformations in the aluminum chloride–nitromethane system. Temperature 80 K: $AlCl_3 + CH_3NO_2 \rightarrow AlCl_3 \cdot CH_3NO_2$ (complex I); $2AlCl_3 + CH_3NO_2 \rightarrow Al_2Cl_6 \cdot CH_3NO_2$ (complex II); $AlCl_3 + 2CH_3NO_2 \rightarrow AlCl_3 \cdot (CH_3NO_2)_2$ (complex III). Temperature 150–230 K: (a) Complex interaction: $Al_2Cl_6 \cdot CH_3NO_2$ (II) $+ CH_3NO_2 \rightarrow 2(AlCl_3 \cdot CH_3NO_2)$ (I). (b) Complex ionization: $AlCl_3 \cdot (CH_3NO_2)_2 \rightarrow AlCl_2(CH_3NO_2)_m{}^+ + AlCl_4{}^-$; $AlCl_3 \cdot CH_3NO_2 \rightarrow AlCl_2(CH_3NO_2)_m{}^+ + AlCl_4{}^-$ $m = 2-4$. (c) Nitromethane catalytic dehydration: $Al_2Cl_6 \cdot CH_3NO_2 \rightarrow AlCl_3 \cdot CH_3NO_2 \rightarrow$; $\rightarrow Al_2Cl_6 \cdot O_2NCH_2CH = NOH + Al(OH)Cl_2 \cdot HCl$.

formation and their transformation under different temperatures and ratios of aluminum chloride:nitromethane.

The formation of dehydration products is supported by infra-red spectral analysis based on quantum mechanical calculations and literature values [18].

It is necessary to note that the catalytic nitromethane dehydration takes place at a low temperature only after the formation of solid $Al_2Cl_6 \cdot CH_3NO_2$ complex.

A probability of the formation of different types of species should be allowed for a consideration of catalytic reactions with aluminum chloride–nitrocompound system involved. Although under equilibrium conditions in solution only one complex is dominated, as a rule, and concentrations of polynuclear complexes may be low, but they can play a key role in catalytic process because of their unusual high activity.

In conclusion, it may be said that the solid state studies using IR spectroscopy yields additional important information on catalyst complexes with reagents, catalytic intermediates, their dynamics and reaction mechanisms. Different chemical properties were found for monomer and dimer aluminum halide complexes. The dimer complexes were more stable and more active as a rule. The results of studies performed on the example of aluminum halide complexes in the solid state at low temperatures can be applicable to understand the nature and properties of homogeneous and heterogeneous catalysts based on aluminum halide under normal conditions. This work shows the need of considering various complex types of aluminum halides with organic nitrocompounds in catalytic reactions. Molecular and ionic complexes revealed by solid state studies may be of interest as possible catalytic intermediates.

Acknowledgements

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