

# Theoretical and low-temperature IR spectroscopic studies of catalytic complexes of aluminum chloride with nitroalkanes and nitrobenzene

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## Abstract

This paper demonstrates the possibilities and advantages of low-temperature infrared (IR) spectroscopy in investigating active labile catalytic complexes, intermediates, and reaction mechanisms, taking aluminum halide complexes as an example. The intermolecular interactions between aluminum chloride and nitromethane, 1-nitropropane and nitrobenzene were studied both by the low-temperature IR spectroscopy and quantum-chemical methods. Three kinds of molecular species have been found in these systems: complexes of monomer  $\text{AlCl}_3$  1:1 and 1:2 composition and 2:1 dimer  $\text{Al}_2\text{Cl}_6$  ones, existing as *trans*- and *gauche*-conformers. Their structure, thermal stability, and catalytic activity were investigated. The aluminum chloride complexes with nitroalkanes are more active than the ones with nitrobenzene in catalytic hydrocarbon cracking. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Complexes between aluminum halides and different organic compounds are very important as catalysts [1–4]. The knowledge of their composition, structure, and stability is very important for understanding the catalysis mechanism. Such investigations under usual conditions (solution, room temperature) are difficult because of rapid equilibria between several complexes with different activities. These equilibria

are frozen out in the solid state and the nature and properties of separate complexes can be investigated. The advantage of the solid state infrared (IR) spectroscopy is best exemplified in the complicated interactions found in the aluminum chloride–nitrocompounds systems.

## 2. Experimental

Aluminum halides (99.99%) were purified by sublimation and stored in sealed ampoules. The investigations were carried out by means of low-temperature IR spectroscopy (4000–400  $\text{cm}^{-1}$ ) of the co-deposits of the reagent vapors

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in a vacuum on the cold copper surface (80 K) using a reactor described in details in Ref. [5]. The aluminum chloride–nitrocompound ratio, order, and temperature of the reagent condensation were varied, and dilution with inert component was used. Samples of a various composition were formed depending on condensation conditions. Obtained films were studied at 80–290 K, the transformations of less stable forms to more stable ones and catalytic reactions were observed. Chromatographic analysis of the reaction products was performed on Chrom-5 chromatograph after warming the samples.

### 3. Results and discussion

#### 3.1. The structure of aluminum chloride thin films

IR spectroscopic monitoring allows permanent control over the reagent behavior. The quantitative spectral analysis of different aluminum chloride condensates at various temperatures allowed the determination of their composition dependence on the dilution extent of comparatively inert hydrocarbon matrix. After  $\text{Al}_2\text{Cl}_6$  vapor deposition at 80 K, the samples were comprised of both dimer molecules and crystal form. Ten-fold dilution gives rise to increased dimer fraction from 40% to 100%.

IR spectroscopy technique allowed to measure kinetics of the disappearance of dimer and formation of the crystal structure of  $\text{AlCl}_3$  in hydrocarbon matrix at 95–150 K. Effective activation energies make up about 6–9 kJ/m. This is consistent with the idea that the metastable molecular form's transformation to the stable crystal takes place with relatively small activation barrier, associated with the necessity of the orientation tuning of molecules.

#### 3.2. Intermolecular interactions in aluminum chloride–nitrocompound systems

The analysis of the observed spectral dependencies on co-deposits' composition established that aluminum chloride may form with nitro-

compounds (nitromethane, 1-nitropropane, and nitrobenzene) at least four kinds of complexes, including unknown earlier molecular complexes of 2:1 and 1:2 compositions, and the 1:1 composition. The interaction between aluminum halide and nitrocompounds already took place at 80 K and gave rise to modifications of their IR spectra. The spectra observed in solid films of  $\text{CH}_3\text{NO}_2\text{-AlCl}_3$  have been discussed in detail previously in Refs. [6–8]. The most shifts were observed in the range of stretch and deformation  $\text{NO}_2$ -modes and stretch  $\text{AlCl}_3$  modes: the  $\text{NO}_2$ -asymmetric stretch rose, while the  $\text{NO}_2$ -symmetric fell under complex formation with aluminum chloride (Table 1). In accordance with quantum-chemical calculations [7,8], asymmetric  $\nu^a(\text{NO}_2)$  are  $1516\text{ cm}^{-1}$  for nitromethane,  $1648\text{ cm}^{-1}$  for  $\text{AlCl}_3 \cdot \text{CH}_3\text{NO}_2$  and  $1641, 1627\text{ cm}^{-1}$  for  $\text{AlCl}_3 \cdot (\text{CH}_3\text{NO}_2)_2$  complexes, and symmetric  $\nu^s(\text{NO}_2)$  are  $1375\text{ cm}^{-1}$  for  $\text{CH}_3\text{NO}_2$ ,  $1334\text{ cm}^{-1}$  for 1:1 and  $1343, 1334\text{ cm}^{-1}$  for 1:2 complexes aluminum chloride with nitromethane, respectively. The situation of stretch of  $\text{AlCl}_3$  modes in complexes of different structures confirmed for nitromethane, by quantum-chemical accounts [7,8], that it depends little on the nature of the nitrocompound. At the same time, the relative shifts of nitrocompound bands have appeared least in the case of nitrobenzene in comparison with nitroalkanes, and this indicates the different nature of intermolecular interaction, with the aromatic electron reservoir effectively taking part, in the case of  $\text{PhNO}_2$ , in coordination.

In the case of nitropropane, it was possible to register complexes not only with different compositions but also with various conformation structure. The main distinctions in the IR spectra of *gauche*- and *trans*-isomers were observed in the range of  $950\text{--}400\text{ cm}^{-1}$ . Their relative stability and possible transformations were studied. Low-temperature co-condensates at 80 K consist of *trans*- and *gauche*-complex isomers; and their ratio does not change after annealing. *Trans*-conformer transforms to a more stable *gauche*-nitropropane at 150–170 K.

Table 1  
IR spectra of nitrocompounds and their complexes with aluminum chloride (80 K)

RNO <sub>2</sub>	$\nu^a(\text{NO}_2), \text{cm}^{-1}$			$\nu^s(\text{NO}_2), \text{cm}^{-1}$			$\nu(\text{Al}-\text{Cl}), \text{cm}^{-1a}$				
	AlCl <sub>3</sub> -RNO <sub>2</sub>			AlCl <sub>3</sub> -RNO <sub>2</sub>			AlCl <sub>3</sub> -RNO <sub>2</sub>				
	RNO <sub>2</sub>	1:2	1:1	2:1	RNO <sub>2</sub>	1:2	1:1	2:1	1:2	1:1	2:1
MeNO <sub>2</sub>	1550 s	1608 m	1610 s	1617 s	1403 s	1356 s	1325 s	1317 s	523 s	546 sh	600 vs
	1560 sh	1590 s				1330 m			505 s	535 s	562 vs
PrNO <sub>2</sub>	1550 s	1603 m	1604 s	1610 s	1387 s	1341 m	1322 s	1316 s	528 s	546 sh	542 vs
	1560 sh	1573 s				1324 m			506 s	538 s	598 vs
PhNO <sub>2</sub>	1519 s	1524 m	1524 s	1526 s	1341 s	1338 s	1328 m	1326 m	534 s	584 m	558 vs
	1514 sh	1519 m				1334 s			500 m	548 sh	555 s
										536 s	547 s

<sup>a</sup> $\nu(\text{Al}-\text{Cl})$  for monomer AlCl<sub>3</sub> above 400 cm<sup>-1</sup> in Ar matrix — 618 cm<sup>-1</sup>[12].

The molecular complexes of aluminum chloride with nitrocompounds show different thermal stability. Complexes of 1:2 composition AlCl<sub>3</sub>(RNO<sub>2</sub>)<sub>2</sub> exist in solid state at 80–170 K solely. Warming it to higher temperatures exceeds the ionic species jet observed only in solutions. [9,10]. Similar complexes may be of interest as catalytic intermediates. The complexes of structures 1:1 and 2:1, synthesized separately, are steady up to 290 K. However, their simultaneous presence at samples causes nitroalkane catalytic dehydration at 170–220 K. Kinetic studies display the intermediate occurrence of ionic species in this processes. Nitrooximes or furoxanes are formed depending on the ratio of reagents, temperature, and dilution. In contrast to nitroalkanes, nitrobenzene–aluminum chloride complexes do not induce dehydration reactions of nitrobenzene.

### 3.3. Quantum-chemical investigations

Ab initio quantum-chemical calculations at the HF/6–31 G level were used to analyze possible structures of the complexes and their spectral data. The results of investigations are demonstrated in Table 2. In accordance with calculations, the coordination in all the complexes occurs through one oxygen atom of nitrocompound. In the 2:1 complex, one of the dimer aluminum chloride bridge bonds is kept.

The geometry of the 1:2 complex is like trigonal bipyramid with coordination number 5 for aluminum atom. The structures of 1:1 aluminum chloride complexes with nitromethane and ni-

Table 2  
Geometry of nitromethane, nitrobenzene, aluminum chloride and their complexes of different composition (HF/6–31 G)

Complex	Bond lengths, Å					Charges, electron	
	$r_{\text{O}-\text{Al}}$	$r_{\text{O}-\text{N}}^a$	$r_{\text{O}-\text{N}}$	$r_{\text{C}-\text{N}}$	$r_{\text{Al}-\text{Cl}}$	$\delta(\text{N})$	$\delta(\text{AlCl}_3)$
PhNO <sub>2</sub>	–	–	1.23	1.45	–	+0.22	–
MeNO <sub>2</sub>	–	–	1.22	1.48	–	+0.33	–
AlCl <sub>3</sub>	–	–	–	–	2.16	–	–
AlCl <sub>3</sub> ·MeNO <sub>2</sub>	1.91	1.27	1.18	1.49	2.20	+0.38	–0.14
AlCl <sub>3</sub> ·PhNO <sub>2</sub>	1.89	1.27	1.19	1.42	2.20	+0.27	–0.14
Al <sub>2</sub> Cl <sub>6</sub> ·MeNO <sub>2</sub>	1.85	1.27	1.18	1.49	2.17	+0.4	–0.14
					2.32 <sup>b</sup>		
					2.44 <sup>b</sup>		
Al <sub>2</sub> Cl <sub>6</sub> ·PhNO <sub>2</sub>	1.86	1.27	1.19	1.42	2.19	+0.27	–0.16
					2.29 <sup>b</sup>		
					2.51 <sup>b</sup>		
AlCl <sub>3</sub> ·2MeNO <sub>2</sub>	2.01	1.25	1.19	1.49	2.24	+0.4	–0.20
	2.01 <sup>c</sup>	1.25 <sup>c</sup>	1.19 <sup>c</sup>	1.49 <sup>c</sup>	2.24	+0.4 <sup>c</sup>	
					2.28		
AlCl <sub>3</sub> ·2PhNO <sub>2</sub>	2.01	1.26	1.20	1.43	2.23	+0.26	–0.25
	2.00 <sup>c</sup>	1.27 <sup>c</sup>	1.20 <sup>c</sup>	1.43 <sup>c</sup>	2.26	+0.27 <sup>c</sup>	
					2.27		

<sup>a</sup>Al-bonded O.

<sup>b</sup>Bridging.

<sup>c</sup>Second RNO<sub>2</sub> molecule.

trobenzene are in agreement with experimental crystal data [11].

A positive charge in all three types of complexes with nitrobenzene is delocalized on an aromatic ring, and on atom of nitrogen it is much less ( $0.27e$ ) than in the appropriate complexes with nitromethane ( $0.4e$ ) (Table 2). Therefore, for complexes with nitroalkanes, it is necessary to expect a higher catalytic activity. The preliminary experiments on low-temperature hydrocarbon cracking have shown that the complexes of aluminum chloride with nitrobenzene are less active than with nitromethane.

Thus, the obtained results display the outlook of using cryospectroscopy and theoretical calculations in the investigation of intermolecular interactions and chemical reaction mechanisms. Molecular and ionic complexes revealed by solid state studies may be of interest as possible catalytic intermediates under normal conditions.

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