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Generation and IR spectra of ionic and molecular complexes of aluminum chloride with *tert*- and *sec*-butyl chlorides

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Sec-butyl and *tert*-butyl cations were first stabilized upon cocondensation of aluminum chloride and haloalkanes (2-chlorobutane and 2-chloro-2-methylpropane, respectively) and their IR spectra and thermal stability investigated. Aluminum chloride anions participating in stabilization of carbenium ions were revealed. Ionic complexes and both 1:1 and 2:1 molecular complexes of reagents were detected and their IR spectra studied. Quantum-chemical calculations at the PBE level of density functional theory with inclusion of electron correlation were employed to optimize the geometric parameters and to determine the vibrational frequencies of aluminum chloride, butyl chlorides, and their complexes of various compositions. The structures of the associates observed were determined on the basis of comparison of the experimental and calculated vibrational spectra.

Key words: infrared spectroscopy, carbocation, molecular complex, aluminum chloride, butyl chloride, low temperature, quantum-chemical calculations, density functional theory.

The "haloalkane—aluminum halide" systems play an important role in organic chemistry. They were used as examples in introducing the concepts of carbenium ions as reactive intermediates of Friedel—Crafts alkylation, electrophilic substitution, cracking, isomerization of paraffins, *etc.*[1—5] Direct experimental observation of long-lived carbocations appeared to be possible only in the early 1960s using strongly acidic solvents (protic superacids);[4—6] however, only the most stable tertiary carbocations were detected. For instance, only *tert*-butyl cation was detected in studies of the reactions of the *n*-butyl, *tert*-butyl, and 2-butyl fluorides with a strong acid SbF_5.[7] This was also observed for *n*-butane and isobutane[8] and *n*-butanol, isobutyl alcohol, and butan-2-ol in $HSO_3F/SbF_5/SO_2$ solution.[9] The 2-butyl cation was first detected by ^1H NMR spectroscopy in the course of low-temperature condensation of 2-chlorobutane and SO_2ClF/SbF_5 at -110 °C.[10] The IR spectra of this species were recorded in studies of low-temperature 2-chlorobutane condensates in SbF_5 matrix.[11] Theoretical studies of the potential energy surface and structure of butyl cations were carried out.[12]

Experimental proofs of generation of carbenium ions under the action of aluminum halides were obtained only for the most stable *tert*-butyl cation.[13] The possibility of stabilization of secondary cations involving aluminum halide was not reported so far. An attempt to stabilize the secondary cation in the low-temperature adsorption of isopropyl bromide on aluminum bromide led to formation of *tert*-butyl cation only, though the interaction of isopropyl bromide with SbF_5 under similar conditions gave an isopropyl cation detected by solid-phase ^{13}C NMR spectroscopy.[14]

In this work both tertiary and secondary carbenium ions were first stabilized by low-temperature cocondensation of aluminum chloride with butyl chlorides. In addition to ionic complexes, molecular complexes of reagents were first detected. We also show that tertiary carbocations can form in nonpolar alkane matrices in the presence of aluminum chloride.

Experimental

Aluminum chloride (Aldrich, 99.99%) was vacuum distilled prior to the preparation of samples. 2-Chloro-2-methylpropane (Merck, 99%) and 2-chlorobutane (Aldrich, 99+%) were used without additional purification. *n*-Octane ("chemically pure" grade) used as a matrix was kept over metallic sodium for several days and then distilled. Purity of starting reagents was monitored by IR spectroscopy and GLC.

IR spectra of solid samples were recorded with a Specord 75 IR and an Infralum FT-801 Fourier spectrometer (Lumex-Sibir, Russia) in the region 4000—400 cm^{-1} using an optical cryostat described elsewhere.[15] Samples were prepared by codeposition of the reagents *in vacuo* on a mirror surface of a copper plate cooled down to 80 K. Cocondensation of aluminum chloride and butyl chlorides was carried out at an $AlCl_3$: BuCl ratio (*n*) from 0.3 to 10 for binary samples and at an C_8H_{18} : $AlCl_3$ ratio from 5 to 50 in *n*-octane matrix. Aluminum

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chloride was condensed by heating vapors to 343—353 K. The hydrocarbon feed rate was controlled by needle valves. The condensation rate was 10^{14} to 10^{16} molecule cm^{-2} s^{-1} and the film thickness was at most 2—15 μm. The temperature was maintained with an accuracy of ±1 K.

Aluminum chloride condensation from the vapor phase under the experimental conditions produces mainly an Al_2Cl_6 dimer characterized by ν(Al—Cl) stretching bands at 617, 478, and 417 cm^{-1} [16,17] when isolated in a hydrocarbon matrix. The IR spectrum of $AlCl_3$ monomer in inert gas matrices in the region $\nu > 400$ cm^{-1} exhibits a single band at 618 cm^{-1}.[17]

Condensation of 2-chlorobutane leads to three conformers, which manifests itself as splitting of some bands in the IR spectra into three components similarly to the case of liquid and argon isolated 2-ClBu.[18,19] The conformer ratio, with predominant contribution of one of them, remains almost unchanged with an increase in temperature.

Calculation Procedure

Quantum-chemical calculations of the structures and vibrational frequencies of the reagents ($AlCl_3$, Al_2Cl_6, Bu^tCl, and 2-ClBu) and their 1 : 1 and 2 : 1 molecular complexes and ionic associates were carried out at the PBE [20] level of density functional theory with inclusion of electron correlation using the PRIRODA program.[21] The one-electron wave functions were expanded with an extended TZ2p basis sets of contracted Gaussian functions of size (311/1) for the H atom, (611111/411/11) for the C atom, and (6111111111/611111/11) for the Al and Cl atoms. Full optimization of the geometry of the systems under study was performed and the harmonic force fields were calculated.

Results and Discussion

System *"aluminum chloride—2-chloro-2-methylpropane"*

Ionic complexes. The IR spectrum of *tert*-butyl cation generated during cocondensation of aluminum chloride with Bu^tCl is shown in Fig. 1. Positions of the characteristic absorption bands are in good agreement with the published data.[6] Our low-temperature thin film studies permitted reliable detection of vibrations in the region 1300 cm^{-1} and revealed a larger shift of the Me stretching band (2780 cm^{-1}) to the low-frequency region compared to 2830 cm^{-1} in solutions. In addition, IR spectra of anions can also be recorded in hydrocarbon matrices at low temperatures. This allows one to obtain a complete spectrum of an ionic complex (ion pair).

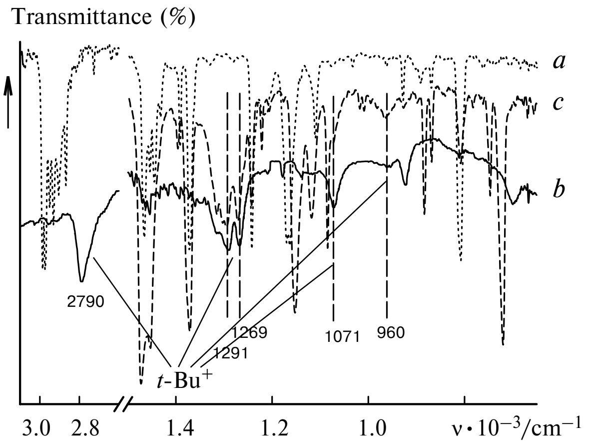


Fig. 1. IR spectra of 2-chloro-2-methylpropane (*a*) and its cocondensates with aluminum chloride (*b*, *c*) in *n*-octane matrix (*c*); $AlCl_3$: Bu^tCl = 10 (*b*) and 1.5 (*c*), C_8H_{18} : $AlCl_3$ = 10 (*c*) at 80 K. Figures are the absorption band frequencies of *tert*-butyl cation (published data[6] for solutions in SbF_5 are as follows: 2830, 1300, 1290, 1070, and 962 cm^{-1}).

Depending on the reagent ratio, $AlCl_4^-$ and $Al_2Cl_7^-$ anions or polynuclear species, usually, $Al_3Cl_{10}^-$ (Table 1) can serve as counterions to the cation under study. In the spectral range studied the $AlCl_4^-$ anion is characterized by a single band of triply degenerate stretching vibrations ν(Al—Cl) at 495 cm^{-1}.[17,22] This band and the spectrum of *tert*-butyl cation can be observed only in the samples containing an excess of butyl chloride at $T > 130$ K. Usually, $Al_2Cl_7^-$ species are detected as counterions to *tert*-butyl cation. The spectrum of $Al_2Cl_7^-$ exhibits bands at 564, 542, and 437 cm^{-1}, being consistent with the published data.[22] The IR spectra of the samples with high aluminum chloride content ($n > 3$) exhibit not only the t-Bu$^+$ cation bands but also new ν(Al—Cl) absorption bands at 589, 537, and 497 cm^{-1}. Most likely, the last-named bands correspond to $Al_3Cl_{10}^-$ anions detected in molten alkali chloroaluminates[23,24] and in ionic liquids[25] by Raman spectroscopy, emission IR spectroscopy, and mass spectrometry.[26] Positions of the $Al_3Cl_{10}^-$ absorption bands we have observed are by and large in agreement with the emission IR spectroscopy data[23] (see Table 1) taking into account a systematic underestimation of the vibrational frequencies of $AlCl_4^-$ and $Al_2Cl_7^-$ anions measured using this technique. The assignment of the spectra we have observed to $Al_3Cl_{10}^-$ anions was confirmed by comparing them with the results of calculations. The calculated IR spectra of $AlCl_4^-$, $Al_2Cl_7^-$, and $Al_3Cl_{10}^-$ anions (see Table 1) are in reasonable agreement with the experimental data, though calculations somewhat underestimate (on the average, by 20 cm^{-1}) the frequencies of the first two anions. According to calculations, the IR spectra of $Al_3Cl_{10}^-$ anion partially overlap with the spectra of $Al_2Cl_7^-$ anion but must exhibit additional bands with frequencies slightly lower than 600 and 500 cm^{-1} (see Table 1), as is observed experimentally. In particular, according to calculations and experimental data, none of the other chloroaluminate anions is characterized by bands in the frequency region above 570 cm^{-1}; the appearance of this band unambiguously indicates generation of a polynuclear ion.

Ionic complex involving *tert*-butyl cation is formed in the course of interaction of reactants at liquid nitrogen

Table 1. Experimental and PBE calculated IR absorption frequencies (ν/cm^{-1}) and intensities* (km mol^{-1}) of stretching vibrations of $Al_nCl_{3n+1}^-$ anions in ionic complexes of t-$Bu^+Al_nCl_{3n+1}^-$ (n = 1—3)

$AlCl_4^-$				$Al_2Cl_7^-$				$Al_3Cl_{10}^-$		
Experiment**			Calculations	Experiment**			Calculations	Experiment**		Calculations
I	II[17,22]	III		I	II[22]	III		I	III	
								587 m	567 m.sh	574 (184)
				564 s	560 s	517 s	537 (187)	545 s.sh	533 s	543 (240)
							536 (231)			541 (240)
				542 s	540 s		521 (64)	537 s		536 (96)
							516 (103)			532 (116)
499 s	495 s	475 s	478 (161)					496 w		480 (61)
			476 (161)							
			475 (160)							
				437 m	430 m	440 w	416 (13)			403 (19)
					383 m	381 m	372 (194)		361 w	383(34)
			326 (0)		330 m	331 m	316 (106)			

* Band intensities are given in parentheses.

** I — this work, II — data taken from Refs 17 and 22, III — emission IR spectra of molten alkali metals.[23]

temperature and is stable up to 250 K. Its spectrum can be recorded not only in the presence of an excess of aluminum chloride ($n > 1$) but also on five- to tenfold dilution with a component of low polarity, *e.g.*, *n*-octane (Fig. 1, *c*) or with an excess of Bu^tCl. In the latter case, however, not only ionic adducts but also adducts of lower polarity are formed.

Molecular complexes. Formation of various associates in the reactions of haloalkanes including Bu^tCl [27] with aluminum halides has long been known.[28] However, spectral characteristics of these species were poorly studied. Information on the vibrational spectra of complexes[29,30] is limited to the region below 600 cm^{-1}. Weakly polarized associates formed in the reaction of aluminum bromide with Bu^tCl in methylene chloride solutions were detected by ^{1}H NMR spectroscopy.[31]

The IR spectra of the molecular complexes of aluminum chloride with Bu^tCl obtained in this work are shown in Fig. 1, *c* and the main vibrational frequencies are listed in Table 2. The molecular associates are characterized by smaller shift of the absorption bands of the initial reagents compared to ionized adducts. The greatest changes were observed in the regions of ν(Al—Cl) stretching vibrations (600—400 cm^{-1}), ν(CCC) asymmetrical vibrations (1200—1300 cm^{-1}), and torsional vibrations of the Me group (1100—1200 cm^{-1}).

Quantum-chemical calculations predict the possibility of formation of the complexes $AlCl_3 \cdot Bu^tCl$ (**1**) and $Al_2Cl_6 \cdot Bu^tCl$ (**2**) with stabilization energies of 14.5 and 26 kcal mol^{-1}, respectively (Table 3). The calculated IR spectra of the molecular complexes are listed in Table 2 an their structures are shown in Fig. 2. The absorption band frequencies of Bu^tCl in the 1 : 1 and 2 : 1 complexes are similar (see Table 2), slight differences must be observed only in the region of torsional vibrations of Me group (1100—1200 cm^{-1}) and in the region of ν(Al—Cl) vibrations (600—400 cm^{-1}). Indeed, positions of the absorption bands of the complexes in these spectral regions depend on the reagent ratio. For instance, the spectra of cocondensates with aluminum chloride exhibit bands at 1165 and 1121 cm^{-1} ($n < 1$) and at 1151 and 1114 cm^{-1} ($n > 1$) instead of a doublet at 1171 and 1163 and a band at 1110 cm^{-1} that are characteristic of free Bu^tCl. Analogously, two new overlapped bands at 550 and 540 cm^{-1} were observed at $n < 1$ in the region of ν(Al—Cl) vibrations, whereas bands at 600, 560 and 500 cm^{-1} (see Table 2) corresponding to the complex $Al_2Cl_6 \cdot Bu^tCl$ (**2**) were recorded in excess of aluminum chloride.

Thus, studies under conditions of restricted molecular mobility allow the complex process of interaction between aluminum chloride and Bu^tCl to be divided into some steps and the following reaction stages to be established (Scheme 1). At 80 K, not only ionic complexes but also molecular complexes **1** and/or **2** are formed depending on the reagent ratio. Usually, the degree of binding of

Scheme 1

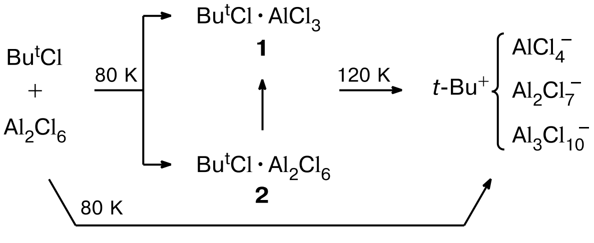


Table 2. Experimental (80 K) and PBE calculated IR absorption frequencies ($\mathrm{cm^{-1}}$) and intensities[a] ($\mathrm{km\ mol^{-1}}$) of 2-chloro-2-methylpropane, aluminum chloride, and their molecular complexes

Free reagents $\mathrm{Bu^tCl}$ and $\mathrm{AlCl_3}$		Complexes						Assignment[b]
		Experiment		Calculations				
Experiment	Calculations	$m\mathrm{AlCl_3 \cdot Bu^tCl}$[c,d]		$\mathrm{AlCl_3 \cdot Bu^tCl}$ (**1**)		$\mathrm{Al_2Cl_6 \cdot Bu^tCl}$ (**2**)		
ν	ν	ν	Δν[e]	ν	Δν[e]	ν	Δν[e]	
2986 vs	3063 (23)	2988 s	+2	3079 (3)	+16	3081 (2)	+18	ν^{as}(Me)
	3063 (23)			3076 (4)	+13	3080 (3)	+17	
2974 vs	3059 (0.1)	2975 s	+1	3072 (5)	+13	3076 (3)	+17	ν^{as}(Me)
	3041 (35)			3047 (8)	+6	3047 (4)	+6	
2970 vs	3035 (6)			3043 (4)	+8	3042 (2)	+7	ν^{as}(Me)
2950 s	3035 (6)	2951 m	+1	3041 (3)	+6	3041 (3)	+6	
2932 s	2970 (32)	2932 m	0	2976 (19)	+6	2974 (11)	+4	ν^{s}(Me)
2905 s	2961 (14)	2905 w		2969 (3)	+8	2966 (1)	+5	ν^{s}(Me)
2868 s	2961 (14)	2864 w	−4	2966 (3)	+5	2965 (1)	+4	
1466 s	1469 (9)	1467 m	−4	1466 (10)	−3	1468 (10)	−1	δ^{as}(Me)
1447 m	1447 (9)	1454 m		1450 (6)	+3	1445 (5)	−2	δ^{as}(Me)
	1447 (9)			1444 (5)	+6	1438 (5)	0	
1443 m	1438 (0.2)	1445 m	+2	1433 (1)	−5	1433 (1)	−5	δ^{as}(Me)
	1438 (0.2)			1429 (2)	+10	1430 (3)	+11	
	1419 (0.1)			1415 (0.2)	−4	1406 (0.4)	−13	
1391 m	1375 (3)			1383 (8)	+8	1375 (11)	+0	δ^{s}(Me)
1373 s	1351 (17)	1371 s	−2	1362 (21)	+12	1354 (31)	+3	δ^{s}(Me)
1369 s	1350 (17)	1320 s	−49	1359 (27)	+9	1351 (26)	+1	δ^{s}(Me)
1243 s	1224 (8)	1270 s	+27	1240 (10)	+16	1245 (12)	+21	$\nu^{\mathrm{as}}(\mathrm{CC_3})$
	1224 (8)	1243 s	0	1235 (17)	+11	1241 (18)	+17	$\nu^{\mathrm{as}}(\mathrm{CC_3})$
1171 vs	1135 (66)	1165 s[c]	−6	1117 (128)	−18			r(Me)
1163 vs		1151 s[d]	−20			1102 (174)	−33	
1110 m	1019 (0.1)	1118 w[c]	+8	1021 (0.1)	+2			r(Me)
		1114 w[d]	+4			1014 (0.1)	−5	
1033 vw	1018 (0.1)			1019 (0.4)	+1	1013 (0.4)	−5	r(Me)
962 w	943 (0.1)	959 w	−3	947 (0.1)	+4	948 (0.1)	+5	r(Me)
928 w	907 (0.1)	924 w	−4	905 (0.2)	−2	892 (0.2)	−15	r(Me)
891 vw	906 (0.1)			900 (0.1)	−6	889 (0.1)	−17	r(Me)
807 vs	793 (10)	807 s	0	744 (13)	−49	770 (17)	−23	$\nu^{\mathrm{s}}(\mathrm{CC_3})$
618[f]	606(326)	600[d]	−18			571 (158)	−35	ν(AlCl)
		560[d]	−58			565 (172)	−41	ν(AlCl)
		550[c,d]	−68	560 (140)	−46	544 (79)	−62	ν(AlCl)
		540[c]	−78	545 (134)	−61			ν(AlCl)
		500[d]	−118			495 (138)	−111	ν(AlCl)
560 vs	545 (30)			467 (19)	−78	444 (5)	−101	ν(CCl)

[a] Band intensities are given in parentheses.

[b] ν and δ are stretching and bending symmetrical (s) and antisymmetrical (as) and r is rocking deformation vibration.

[c] $m = 1$.

[d] $m = 2$.

[e] Frequency difference between the complex and free reagent.

[f] For $\mathrm{AlCl_3}$ monomer in the region above 400 $\mathrm{cm^{-1}}$ in Ar matrix.[17]

reagents during cocondensation is lower than 100% and increases as the temperature increases to 100—130 K. The spectra of the samples containing an excess of aluminum chloride ($n > 1$) are characterized by simultaneous disappearance of the bands of molecular complexes and an increase the band intensities of ionic adducts with an increase in temperature. The lack of aluminum chloride ($n < 1$) or dilution with an inert component cause the molecular complexes to be stable up to 200 K.

System "aluminum chloride—2-chlorobutane"

In contrast to 2-chloro-2-methylpropane that forms an ionic complex with aluminum chloride in the course of

Table 3. PBE calculated total energies (E) of 2-chlorobutane, 2-chloro-2-methylpropane, aluminum chloride monomer and dimer, and their complexes **1—4**; and energies of formation of the complexes from the starting reagents without (ΔE) and with allowance for aluminum chloride dimerization ($\Delta E'$)

Compound	$-E$/a.u.	$-\Delta E$	$-\Delta E'$
		kcal mol^{-1}	
2-ClBu	617.72179412	—	—
Bu^{t}Cl	617.72561008	—	—
$AlCl_3$	1622.62471871	—	—
Al_2Cl_6	3245.29244856	27.0	—
$AlCl_3 \cdot Bu^tCl$ (**1**)	2240.37345011	14.5	1.0
$Al_2Cl_6 \cdot Bu^tCl$ (**2**)	3863.01652326	26.0	−1.0
$AlCl_3 \cdot$ 2-ClBu (**3**)	2240.37126477	15.5	2.0
$Al_2Cl_6 \cdot$ 2-ClBu (**4**)	3863.01609512	28.2	1.2

condensation of the starting reagents, the formation of the secondary carbocation at 80 K is complicated and occurs only at elevated temperatures. The initial stage of the interaction of Al_2Cl_6 with 2-chlorobutane involves formation of molecular complexes unknown earlier.

Molecular complexes. Complexation manifests itself as disappearance of some absorption bands of the starting reagents (at 1298, 1237, 1076, 617, 603, 477, 418 cm^{-1}, *etc.*, see Fig. 3, *a* and Fig. 4, *a*) and appearance of new bands at 1282, 1224, 1069, 571, and 555 cm^{-1} (see Fig. 3, *b* and Fig. 4, *b*, *c*) in the IR spectra. Varying the $AlCl_3$/2-ClBu ratio from $n = 5$ to 0.1 in the cocondensates leads to some changes in the vibrational spectra of re-

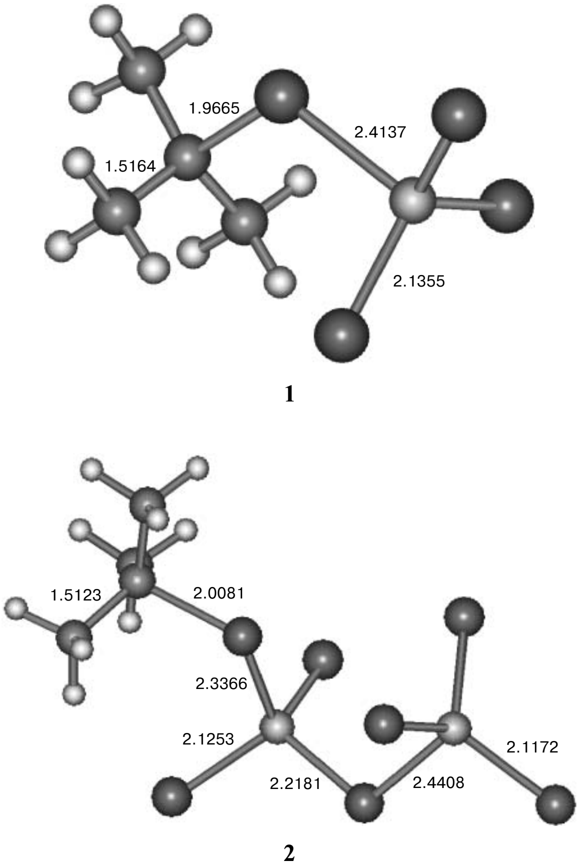


Fig. 2. PBE calculated equilibrium structures of molecular complexes $AlCl_3 \cdot Bu^tCl$ (**1**) and $Al_2Cl_6 \cdot Bu^tCl$ (**2**).

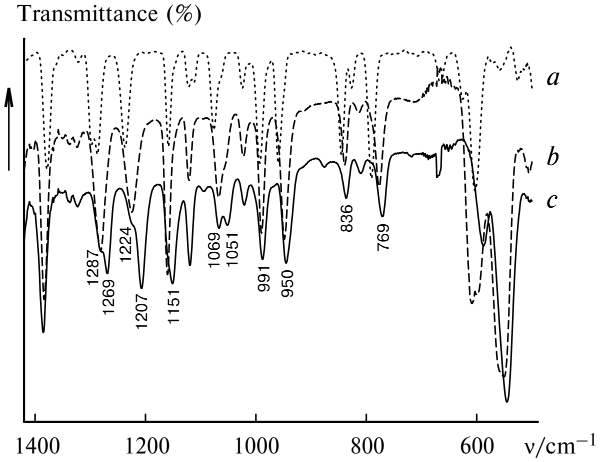


Fig. 3. IR spectra of 2-chlorobutane (*a*) and its cocondensates with aluminum chloride (*b*, *c*) at 80 K (*a*, *b*) and 150 K (*c*); $AlCl_3$: 2-ClBu = 3.

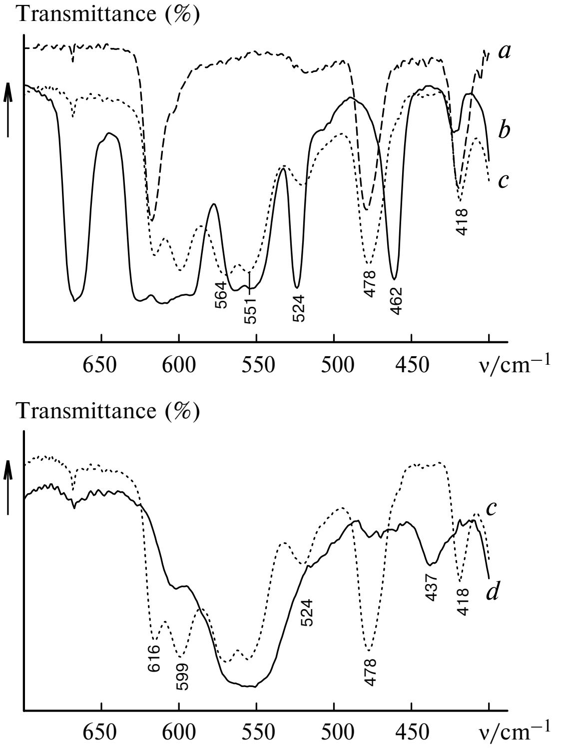


Fig. 4. IR spectra of Al_2Cl_6 (*a*) and its cocondensates with 2-chlorobutane (*b—d*) at different reagent ratios and temperatures: $AlCl_3$: BuCl = 0.1 (*b*), 1.5 (*c*, *d*) at 80 K (*a—c*) and 150 K (*d*).

Table 4. Experimental (80 K) and PBE calculated IR absorption frequencies (cm^{-1}) and intensities[a] (km mol^{-1}) of 2-chlorobutane, AlCl$_3$, and their molecular complexes AlCl$_3$·2-ClBu (**3**) and Al$_2$Cl$_6$·2-ClBu (**4**)

Free reagents 2-ClBu and AlCl$_3$		Complexes				Assignment[b]
		AlCl$_3$·2-ClBu (**3**)		Al$_2$Cl$_6$·2-ClBu (**4**)		
Experiment	Calculations	Experiment	Calculations	Experiment	Calculations	
2972 s	3062 (16)	2975 s	3075 (3)	2977 s	3078 (2)	ν(Me)
	3045 (30)		3056 (16)		3055 (12)	
2938 s	3039 (31)	2939 s	3050 (21)	2939 s	3054 (13)	ν(Me)
	3035 (26)		3044 (5)		3043 (1)	
2929 s	3014 (2)	2926 m	2989 (6)	2927 s	2991 (16)	ν(CH$_2$)
2917 m	2999 (5)	2917 w	3028 (1)	2914 m	3025 (27)	ν(CH)
2878 m	2970 (23)	2878 m	2979 (12)	2879 m	2981 (10)	ν(Me)
	2965 (15)		2971 (11)		2971 (6)	
2846 w	2971 (13)	2847 w	2944 (11)	2854 w	2943 (7)	ν(CH$_2$)
1461 s	1465 (7)	1460 s	1455 (15)	1458 s	1456 (12)	δ(Me)
	1454 (7)		1450 (13)		1451 (12)	
1455 s	1450 (6)	1455 s	1446 (7)	1452 s	1448 (5)	δ(Me)
1443 s	1444 (13)	1440 s	1432 (8)	1440 s	1432 (8)	δ(Me)
1432 m.sh	1435 (1)		1416 (2)		1411 (4)	δ(CH$_2$)
1378 s	1359 (11)	1381 s	1373 (6)	1383 s	1370 (6)	δ(Me)
1362 w	1352 (6)		1361 (14)		1363 (17)	δ(Me)
1321 vw	1330 (1)	1323 vw	1348 (1)	1324 vw	1355 (2)	χ (CH)
1298 s	1303 (3)	1282 s	1277 (14)	1280 s	1277 (4)	w(CH$_2$)
1287 s	1251 (1)	1287 s	1266 (6)	1288 s	1267 (27)	sc(CH$_2$), χ_i(CH)
1237 s	1214 (19)	1224 s	1215 (9)	1224 s	1217 (16)	χ_i(CH)
1158 s	1143 (13)	1160 s	1143 (15)	1160 s	1145 (20)	ν(CC)
1122 m	1125 (1)	1122 m	1108 (3)	1122 m	1112 (4)	ν(CC)
1076 s	1045 (12)	1069 s	1054 (8)	1067 m	1048 (6)	ν(CC), r(Me)
1025 m	1002 (6)	1024 m	1015 (6)	1022 m	1013 (9)	ν(CC)
993 s	958 (5)	991 s	972 (16)	989 s	970 (12)	r(Me)
959 s	935 (9)	950 s	937 (11)	948 s	931 (13)	r(Me)
844 s	831 (9)	843 s	825 (6)	838 s	825 (7)	ν(CC)
826 w		815 m		813 m		
791 s	767 (4)	778 s	765 (18)	776 s	757 (21)	r(CH$_2$)
618[c]	606 (162)			596 m.br	595 (147)	ν(Al—Cl)
		563 m.br	568 (147)	570 m.br	568 (136)	ν(Al—Cl)
		551 m.br	545 (131)	555 m.br	537 (155)	ν(Al—Cl)
				520 w	492 (71)	ν(Al—Cl)
603 vs	652 (29)		512 (22)	476 m	479 (50)	ν(CCl)
	408 (1)		443 (2)		445 (4)	γ(CCC)
	362 (31)		362 (33)		379 (51)	ν(CCl), γ(CCCl)
			330 (41)			ν(Al—Cl)
	314		312			γ(CCCl)

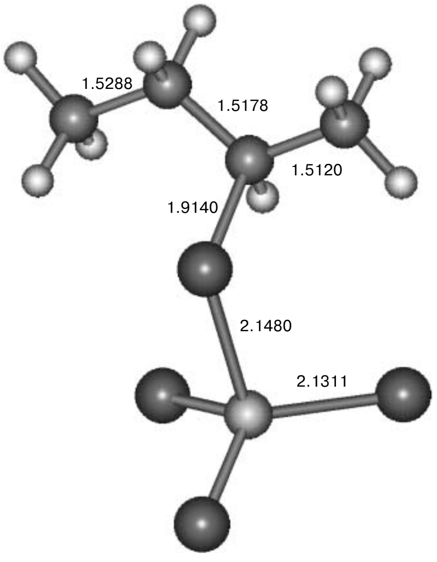
[a] Band intensities are given in parentheses.

[b] ν is stretching, δ and γ are bending, χ and χ_i are out-of-plane and in-plane deformation, r is rocking deformation, sc is scissoring, and w is wagging vibration.

[c] For AlCl$_3$ monomer in the region $\nu > 400$ cm^{-1} in Ar matrix.[17]

agents (Table 4), which indicates formation of associates of different compositions.

Quantum-chemical calculations predict the possibility of formation of the donor-acceptor complexes AlCl$_3$·2-ClBu (**3**) and Al$_2$Cl$_6$·2-ClBu (**4**) with stabilization energies of 15 and 28 kcal mol^{-1}, respectively (see Table 3). The calculated IR spectra of these molecular complexes are listed in Table 4 and their structures are shown in Fig. 5. The observed frequency shifts of the bands of the 2-ClBu constituent of the complexes are in reasonable agreement with the calculated values (see Table 4). The greatest changes were found in the region 1300—1200 cm^{-1} corresponding to the Me bending vibrations and CCH in-plane deformation vibrations. The band at 1298 cm^{-1} is shifted by –(16—20) cm^{-1}, which is consistent with the calculated value, –26 cm^{-1}. Accord-



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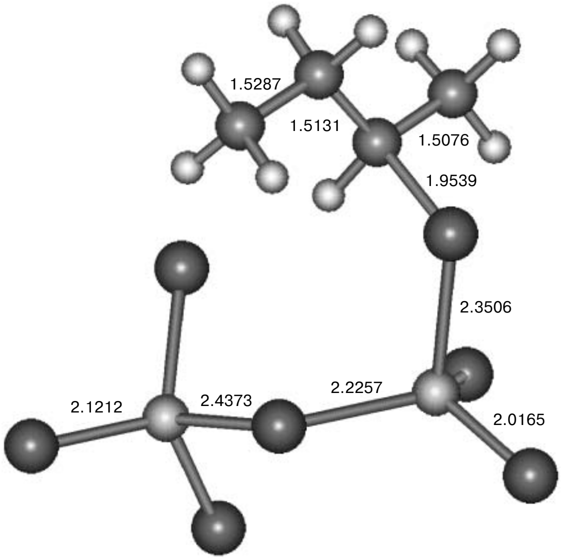


4

Fig. 5. PBE calculated equilibrium structures of molecular complexes $AlCl_3 \cdot 2\text{-}ClBu$ (**3**) and $Al_2Cl_6 \cdot 2\text{-}ClBu$ (**4**).

ing to calculations (see Table 4), the IR spectra of complexes **3** and **4** must not be strongly different, the frequency difference being at most 5 cm^{-1}, as is actually observed.

In the spectral region corresponding to Al—Cl vibrations positions of absorption bands also depend on the reagent ratio *n* (see Fig. 4), though here spectral analysis is complicated by the presence of Al_2Cl_6 bands at 617, 478, and 418 cm^{-1} and free 2-ClBu bands at 603, 524, 462, and 422 cm^{-1}. At $n < 1$, the spectra of cocondensates of aluminum chloride and 2-chlorobutane exhibit an intense doublet at 564 and 551 cm^{-1} (see Fig. 4, *b*, *c*). If aluminum chloride is taken in excess ($n > 1$), new absorption bands at 598, 570, 555, and 520 cm^{-1} are observed. The fact that the spectral pattern depends on the reagent ratio indicates formation of molecular complexes of different compositions. The vibrational frequencies observed are in agreement with those calculated for complexes **3** and **4** (see Table 4).

As the temperature increases, molecular complexes are transformed into new associates characterized by stronger changes in the vibrational spectra compared to the spectra of the starting reagents.

Ionic complexes. The IR spectra in the region of ν(Al—Cl) vibrations are shown in Fig. 4, *c*, *d*. As the temperature increases from 80 to 150 K, the ν(Al—Cl) band intensities of molecular complex **4** (at 599, 570, 555 cm^{-1}, *etc.*) decrease while the intensities of the new absorption bands (590, 555 br, 437 cm^{-1}) characterizing the $Al_2Cl_7^-$ and $Al_3Cl_{10}^-$ anions (*cf.* Table 1) increase. Simultaneously, the spectrum in the high-frequency region changes (see Fig. 3, *c*), namely, the absorption band intensities of both free 2-chlorobutane and donor-acceptor complexes decrease and new absorption bands appear (at 1269, 1207, 1051, 836 cm^{-1}, *etc.*), which should likely be assigned to vibrations of the carbocationic fragment of the ionic complex.

The frequencies of the bands of the complexes detected at $T \geq 150$ K are listed in Table 5. Earlier,[11] the IR spectrum of 2-ClBu similar to that observed in this work was recorded in SbF_5 matrix in the same temperature range.[11] A comparison with the ^1H and ^{13}C NMR spectroscopy data[10,32] and with the results of quantum-chemical calculations[12] allowed[11,12] the IR absorption bands obtained to be assigned to the vibrational spectra of secondary butyl cation, *s*-Bu^+. In our case the *s*-Bu^+ cation is also stabilized in the presence of aluminum chloride.

The formation of ionic complexes in the reaction of Al_2Cl_6 with 2-chlorobutane is evidenced by simultaneous detection of an organic cation, whose spectrum is similar to that of the *sec*-Bu^+ cation, and the chloroaluminate anion. For comparison, Fig. 6 presents the spectra of ionic complexes of Bu^tCl and 2-ClBu with $AlCl_3$. Both systems exhibit nearly identical spectra in the region below 600 cm^{-1}, which corresponds to Al—Cl vibrations. In this case, in a large excess of Al_2Cl_6 ($n > 3$), these are mainly the spectra of $Al_3Cl_{10}^-$ anion. At smaller *n* values, $Al_2Cl_7^-$ anions dominate (see, *e.g.*, Fig. 4, *d*).

The spectra of both systems observed in the high-frequency region are different. A characteristic feature of the spectrum of *t*-Bu^+ cation (see Fig. 6, *a*) is a marked decrease in the C—H vibrational frequency toward ~2800 cm^{-1}. As to the *s*-Bu^+ cation, a similar ν(CH) frequency shift can be expected only for the classical planar structure of this cation; otherwise, the spectrum of the cation in this region will not be strongly different from the spectrum of 2-ClBu (see below). Ionic complexes de-

Table 5. Experimental and calculated vibrational frequencies (cm^{-1}) and band intensities* ($km\ mol^{-1}$) of different structures of *sec*-butyl cation (*s*-Bu^+) and calculated relative energies of their formation ($kcal\ mol^{-1}$)

Experiment (150 K, matrix)		Calculations		
		A	**B**	**C**
$AlCl_3$	SbF_5[11]	−0.813	−0.079	0
2978 s	3053 s	3157 (11)	3095 (6)	3088 (0.1)
		3135 (4)	3086 (1)	3088 (6)
2941 m	2988 m	3095 (3)	3067 (3)	3063 (5)
2916 m	2937 m	3071 (2)	3041 (2)	3049 (0.2)
		3066 (3)	3017 (3)	3031 (5)
2904 m		3034 (14)	2992 (2)	3031 (2)
2883 m		3019 (3)	2979 (22)	2960 (5)
		2917 (13)	2848 (88)	2960 (40)
2849 m	2175 m	2900 (66)	2602 (117)	2096 (22)
	1552 m		1497 (50)	1527 (10)
1452 s	1454 vs	1507 (22)	1453 (22)	1441 (28)
1440 s	1444 vs	1450 (18)	1436 (18)	1424 (24)
		1420 (24)	1415 (18)	1412 (17)
		1409 (24)	1370 (6)	1409 (7)
		1394 (9)	1359 (19)	1351 (8)
1387 s	1375 vs	1360 (29)	1286 (21)	1347 (45)
1280 s	1306 s	1320 (38)	1272 (54)	1296 (3)
1269 s	1281 s	1301 (8)	1256 (45)	1284 (2)
1207 s	1213 m	1259 (6)	1219 (32)	1181 (15)
1151 s	1157 m	1200 (3)	1172 (3)	1156 (1)
1119 m	1122 w	1163 (12)	1073 (19)	1081 (3)
1049 s	1059 m	1068 (5)	1043 (4)	1073 (7)
1020 m	1022 w	1021 (20)		1032 (10)
987 s	991 s	957 (12)	1028 (52)	987 (18)
944 s	964 vs	927 (6)	966 (26)	970 (11)
935 s	899 vs	899 (23)	863 (2)	840 (1)
836 s	835 s	889 (7)	771 (8)	748 (21)
809 m		801 (46)	725 (27)	
769 s		623 (60)		
		419 (10)	479 (24)	480 (0.1)
		363 (13)	409 (57)	329 (265)
		237 (2)	261 (6)	256 (0.1)

Note: **A** is the structure with methyl bridge, **B** is the classical planar structure, and **C** is the structure with hydrogen bridge.

* Band intensities are given in parentheses.

tected in the system 2-ClBu—Al_2Cl_6 contain no *tert*-butyl cation.

The structure of sec-butyl cation

Our quantum-chemical calculations predict the possibility of formation of three stable structures of the *s*-Bu^+ cation (Fig. 7). According to calculations (see Table 5), structure **A** with a Me bridge is the most stable. The classical planar carbocation structure (**B**) and the *s*-Bu^+ structure with symmetric hydrogen bridge (**C**) have similar energies but are less energetically favorable (however, the energy difference is less than 1 $kcal\ mol^{-1}$). Analogous

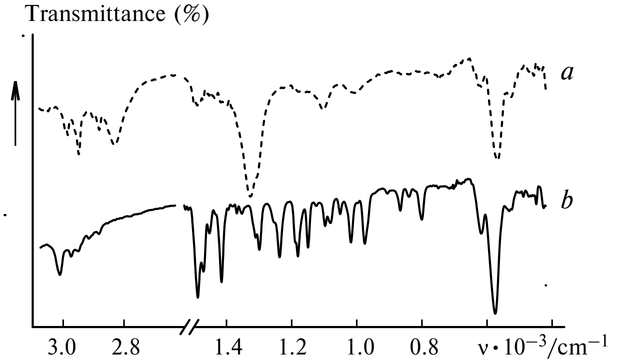


Fig. 6. IR spectra of Al_2Cl_6 cocondensates with 2-chloro-2-methylpropane (*a*) and 2-chlorobutane (*b*) at a $AlCl_3$: BuCl ratio of 3.5 (T = 150 K).

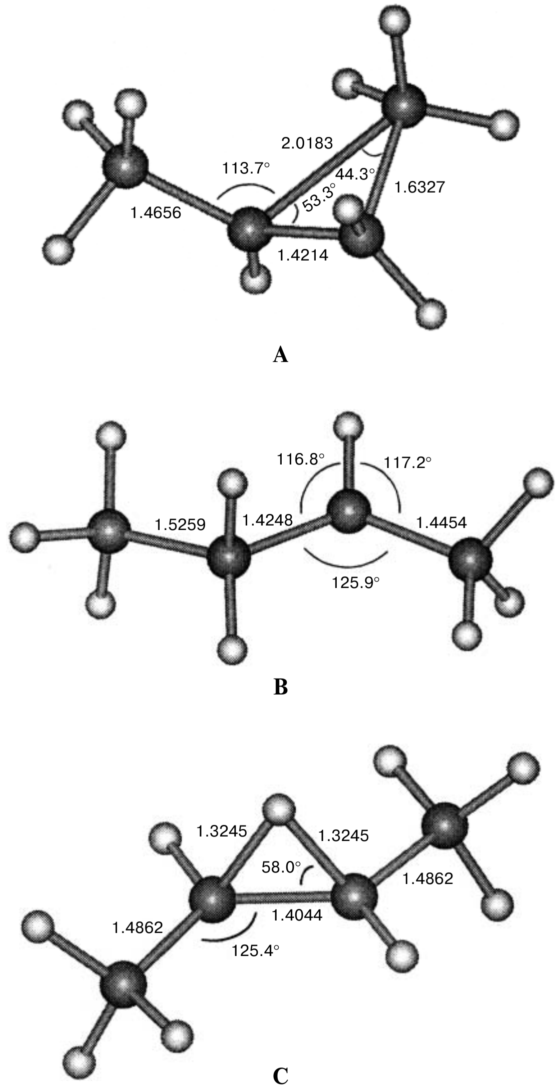


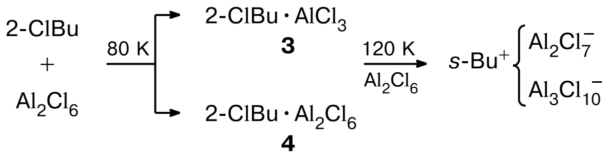
Fig. 7. Different PBE calculated structures of *sec*-butyl cation: structure with methyl bridge (**A**), classical planar open-chain structure (**B**), and structure with hydrogen bridge (**C**).

conclusions that the structures **A—C** of *s*-Bu^+ cation have similar energies were reported in ^1H and ^{13}C NMR studies,[32—34] ESCA studies,[35] and *ab initio* theoretical studies[12] (in the last-mentioned case preferableness of the structure **A** or **C** depends on the level of theory employed in particular calculations).

The IR spectra calculated in this work for different structures of *sec*-butyl cation are also listed in Table 5. The band frequencies in these spectra are similar, being fundamentally different only in the region above 2000 cm^{-1}. Namely, the appearance of a band in the region 2100 cm^{-1} was predicted for structure **C**, an intense band at 2600 cm^{-1} was predicted for the planar *s*-Bu^+ cation structure (**B**), and no new bands in these spectral regions were predicted only for structure **A**. A comparison of the experimental frequencies of *s*-Bu^+ cation in different media with the calculated values (see Table 5) shows that structure **A** is mainly stabilized in the $AlCl_3$ matrix in contrast to the SbF_5 matrix where structure **C** is most probable[11,12] (though ESCA studies[35] give preference to structure **A**). Generally, it is more appropriate to consider a dynamic equilibrium between different structures of *s*-Bu^+ cation, because the energy difference between them is small.

Thus, depending on the reagent ratio, cocondensation of Al_2Cl_6 and 2-chlorobutane at 80 K leads to molecular complexes **3** and **4** that are stable up to 120 K. As the temperature increases, they are transformed into ionic associates. The pathways of formation and transformation of the complexes of $AlCl_3$ with 2-ClBu can be summarized in Scheme 2.

Scheme 2



Thermal stability and transformation of butyl cations

A comparison of the character of intermolecular interactions of $AlCl_3$ with 2-ClBu and Bu^tCl (see Schemes 1 and 2) shows that no ionic complexes are formed in the reaction at 80 K in the former case and ionization involves transient formation of molecular complexes (**3** or **4**) that are more stable than corresponding Bu^tCl complexes (**1** and **2**). This first of all concerns the molecular associates with Al_2Cl_6. Complexes **2** can be experimentally detected only at 80 K; they are transformed into more stable associates **1** or into ionic complexes on heating. Complexes **3** and **4** can be detected at $T > 150$ K.

The *sec*-butyl cation we have synthesized under the action of aluminum chloride is stable between 130 and 180 K in contrast to *tert*-butyl cation that is stable in the temperature interval 80—250 K. It should be noted that no isomerization of *s*-Bu^+ into *t*-Bu^+ was observed in the thermal stability region of the *sec*-butyl cation in the $AlCl_3$ matrix. Though the difference between the formation energies of the *sec*- and *tert*-butyl cations is 14.5 kcal mol^{-1},[36] the activation energy for this transformation is rather high (18 kcal mol^{-1} [10]) because the process requires transient formation of energetically unfavorable primary cation. Therefore, heating to at least 233 K was necessary for *s*-Bu^+ isomerization to occur in SbF_5-based media.[10,11] In our case, this reaction can not proceed because *s*-Bu^+ is stable only below 180 K.

Thus, *sec*-butyl and *tert*-butyl cations were first stabilized upon cocondensation of aluminum chloride and haloalkanes and their IR spectra and thermal stability investigated. Aluminum chloride anions participating in stabilization of carbenium ions were revealed.

The possibility of generation of the secondary carbocation under the action of aluminum halides is important when considering the reaction mechanisms involving these catalysts.

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