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The structure of equimolar complexes of acyl halides with Lewis acids

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ABSTRACT. The results of studies on the structures of equimolar complexes of acyl halides with Lewis acids in the solid state and in solutions are surveyed. The methods for the identification of acylium salts and donor–acceptor complexes as well as the factors influencing the equilibrium between them are examined. Communications reporting the formation of complexes of other types in acyl halide–Lewis acid systems are reported and are discussed critically.

The bibliography includes 102 references.

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I. Introduction

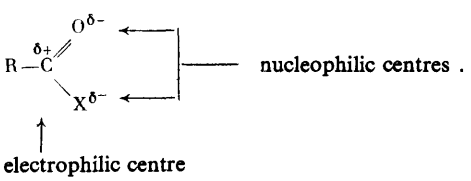
The discovery by Friedel and Crafts towards the end of the past century of the activating effect of aluminium chloride on acid halides initiated the fruitful application of the $RCOX-MX_n$ systems (RCOX = acyl halide, MX_n = Lewis acid) in organic synthesis. The continued interest in these systems is associated mainly with their use in the acylation of arenes, which is a classical method of synthesis of aromatic ketones.[1–4] The systems $RCOX.MX_n$ have also found applications in reactions with olefins, acetylenes, and other unsaturated compounds, which lead to saturated and unsaturated ketones, aliphatic haloketones, oxonium and pyrylium salts, etc.[2,5,6] The reactions of the complexes $RCOX.MX_n$ with unsaturated compounds have not lost their immediate interest, the region of their application is being expanded, and the study of their mechanisms is being continued at the present time.[5–16]

By virtue of studies on the $RCOX.MX_n$ systems, initiated as early as the beginning of the century and developed to the greatest extent in 1960's–1970's by Susz, Cook, Olah, Carpentier, Boer, Weiss, Corriu, and others, considerable advances have been achieved in the understanding of the mechanism of the interaction of acyl halides with Lewis acids and in the determination of the structures of the complexes formed under these conditions. However, even now many important problems concerning the structures of these complexes remain unsolved.

The structure of the complexes $RCOX.MX_n$ has been the subject of many reviews and chapters in monographs.[2,5,7,17,18] Unfortunately none of them is sufficiently complete and many unsolved problems and contradictory data have not been dealt with in the reviews quoted. Such reviews are lacking in the Soviet literature. Furthermore, during the last decade the interest in the complexes of acyl halides with Lewis acids has increased greatly because it has been found that the conversion of the complexes $RCOX.MX_n$ into the complexes $RCOX.2MX_n$ is accompanied by an abrupt increase in their reactivity. The complexes $RCOX.2MX_n$, which have been called aprotic organic superacids, have higher reactivities in reactions with alkanes and cycloalkanes than all the known systems based on AlX_3 (including $RCOX.MX_n$) and also, as a rule, the strongest protic superacids.[19] Taking the foregoing into account, we believe it useful to publish a review on this topic. The structure of aprotic organic superacids (the complexes $RCOX.2AlX_3$), the types of reactions of alkanes and cycloalkanes initiated by them, and also the nature of the superacid properties of these complexes will not be considered here. That range of problems merits an independent review.

II. Interaction of acyl halides with Lewis acids. The structures of the postulated complexes

Acyl halides are amphoteric and are capable of reacting as both Lewis acid and Lewis bases:



The electrophilic centre of the molecule is the carbonyl carbon atom, while the nucleophilic centres are the oxygen and halogen atoms, the greatest electron density being concentrated on the oxygen atom.[5,20]

In conformity with their nucleophilic nature, acyl halides react with a wide range of Lewis acids. The first well characterised complex having the composition $RCOX.MX_n$ was obtained in 1943 by Seel[21] in the reaction of AcF and BF_3. On the basis of the results of elemental analysis and conductimetric measurements, the ionic salt structure $CH_3CO^{\oplus}BF_4^{\ominus}$ was attributed to the complex. It was

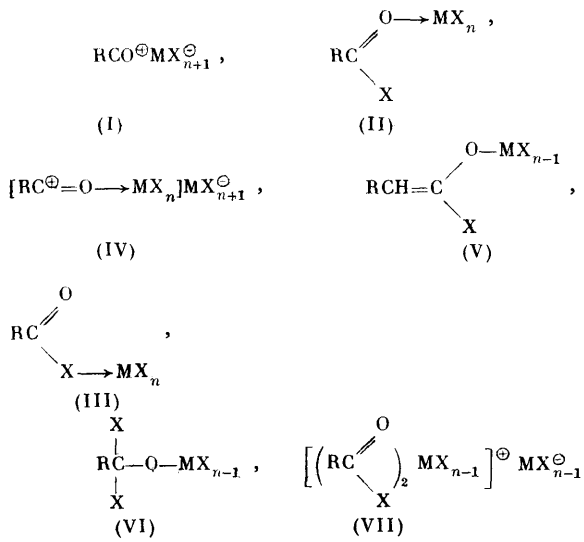
subsequently confirmed by other physicochemical methods. Certain 1:1 $RCOX.MX_n$ complexes and their constants are presented in Table 1.

Table 1. The properties of certain adducts $RCOX.MX_n$ (1:1).

Adduct	M.p., °C	Decomp. temp., °C	Refs.
$CH_3COCl\cdot AlCl_3$	65	–	[22]
$2\text{-}CH_3C_6H_4COCl\cdot AlCl_3$	55	–	[23]
$2,6\text{-}(CH_3)_2C_6H_3COCl\cdot AlCl_3$	82	–	[23]
$CH_3COCl\cdot GaCl_3$	86	–	[24]
$PhCOCl\cdot GaCl_3$	47	–	[24]
$CH_3COCl\cdot BCl_3$		–50	[24]
$CH_3COF\cdot BF_3$	–	20	[21]
$PhCOF\cdot BF_3$	–	–30	[25]
$CH_3COCl\cdot TiCl_4$	20	–	[26]
$C_3H_7COCl\cdot TiCl_4$	–4	–	[26]
$2\text{-}CH_3C_6H_4COCl\cdot TiCl_4$	70	–	[23]
$CH_3COF\cdot AsF_5$	175	–	[25]
$PhCOF\cdot AsF_5$	158	–	[25]
$CH_3COF\cdot PF_5$	–	30	[25]
$PhCOF\cdot PF_5$	–	–15	[25]
$CH_3COF\cdot SbF_5$	173	–	[25]
$PhCOF\cdot SbF_5$	150	–	[25]
$(CH_3)_3CCOF\cdot SbF_5$		20	[27]
$F_2CHCOF\cdot SbF_5$	–	50	[28]

The reactions of acyl halides with the halides of Group III–V elements (BF_3, BCl_3, $AlCl_3$, $AlBr_3$, $GaCl_3$, $GaBr_3$, $TiCl_4$, SbF_5, $SbCl_5$, AsF_5, PF_5, etc.), which lead, as a rule, to the equimolar adducts $RCOX.MX_n$, have been the most thoroughly investigated. The structures proposed for the adducts are presented in Scheme 1 below.[17]

Scheme 1

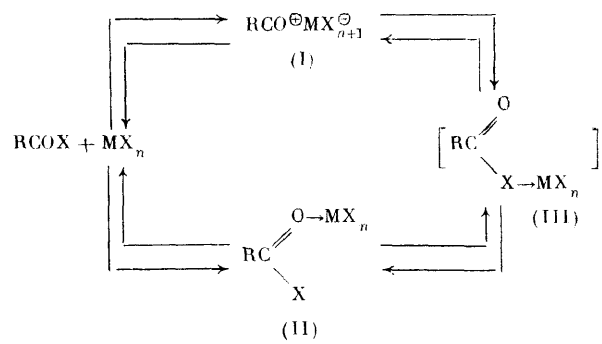


It has now been shown by IR and NMR spectroscopy and also by X-ray diffraction that the stable 1:1 adducts $RCOX.MX_n$ exist in one of two forms: either as acylium salts (I) or as coordination complexes (II).[1,5–7,17,18] None of the postulated complexes (II)–(VII) has been detected in the study of a wide range of $RCOX.MX_n$ systems. In the study of the $FCH_2COF-SbF_5$ system by NMR, Olah[28] demonstrated in only one instance that three complexes coexist simultaneously in the system and attributed to them the structures of complexes (I), (II), and (III), (Scheme 2).[28] However, the final conclusion concerning the existence of type (III) complexes can apparently be reached only if its structure can be demonstrated by direct method.

The conversion of acyl halides by Lewis acids into the "Illary complexes" (V) has been postulated.[29,30] Susz and co-workers[31] investigated very carefully the possibility of the presence of the "Illary complex" in the $AcCl.AlCl_3$ system and showed that it is not formed at room temperature. Thus type (V) complexes as well as the other hypothetical complexes (IV), (VI), and (VII) could not be detected in any of the systems investigated.

The formation of the acylium salt (I) and of the coordination complex (II) corresponds to two possible pathways in the reactions of acyl halides with a Lewis acid. Attack on the first nucleophilic centre of the RCOX molecule (the halogen atom), accompanied by the heterolysis of the C–X bond, leads to the acylium salts (I), whilst attack on the second nucleophilic centre (the oxygen atom of the carbonyl group) leads to the formation of a donor–acceptor complex (II) as a result of the coordination of MX_n to the *n*-electron pair of the oxygen atom.

Scheme 2



The position of the equilibrium (I) ⇄ (II) depends on many factors: the strength of the Lewis acid MX_n, the nature of the groups R and X in RCOX, temperature, and (in solutions) also on the nature of the solvent (see Section VI).

All these factors determine whether or not the $RCOX.MX_n$ system exists exclusively as one of the complexes (I) or (II) or whether an equilibrium is established in which both structures contribute appreciably.

III. Acetylium cations. Quantum-chemical calculations

The simplest ionic products of the interaction of acyl halides with Lewis acids are acetylium salts containing the cation $CH_3CO^{\oplus}$, because the first member of the homologous series — the formylium cation $HCO^{\oplus}$ — could not be obtained as part of the composition of a stable compound.[32]

The cation having the empirical formula $C_2H_3O^{\oplus}$ can have a series of isomeric structures,[33–35] but only the cation $CH_3C^{\oplus}=O$ and the 1-hydroxyvinyl cation $CH_2=C^{\oplus}-OH$, which exist in the form of stable long-lived species, have been detected directly. Calculations

of the energies of the ions $C_2H_3O^{\oplus}$ by the *ab initio* method showed that the cation $CH_3C^{\oplus}=O$ corresponds to the minimum energy and that the ion $CH_2=C^{\oplus}-OH$ is the second as regards stability.[34,36]

The acetyl cation can be regarded as a hybrid of the three resonance structures (A'), (A''), and (A'''), which correspond to different locations of the positive charge (Scheme 3). In the carboxonium ion (A') the charge is concentrated on the oxygen atom, in the oxocarbenium ion (A'') it is concentrated on the carbonyl carbon atom, while in the ion of the C-protonated ketene (A''') it is concentrated on the hydrogen atoms of the methyl group (hyperconjugation of the C–H β-bonds and the cationic centre):

Scheme 3

$$\underset{(A')}{CH_3C{\equiv}O^{\oplus}} \longleftrightarrow \underset{(A'')}{CH_3C^{\oplus}{=}O} \overset{H^{\oplus}}{\longleftrightarrow} \underset{(A''')}{CH_2{=}C{=}O}\ .$$

The foregoing is valid also for other ionic structures $RCO^{\oplus}$. The contribution of each resonance form to the real structure of the ion $RCO^{\oplus}$ depends to a large extent on the nature of the group R linked to the carbonyl and will be considered in Sections (IV.1) and (V.2).

IV The structure of equimolar complexes of acyl halides with Lewis acids according to X-ray diffraction data

1. The structure of acylium salts $RCO^{\oplus}MX^{\ominus}_{n+1}$

The existence of the ionic complexes (I) and the donor–acceptor complex (II) has been demonstrated by the direct X-ray diffraction method.[37–49] The first crystallographic determination of the structure of an acylium salt was achieved for acetylium hexafluoroantimonate by Boer.[45,46] Although the accuracy of this study, carried out by a photomethod, and the conclusions concerning the electron density distribution obtained on its basis are doubtful,[17] its principal result, indicating a truly ionic structure of the acylium salt, is incontrovertible.

Fig. 1 presents the structure of the acylium salt. Table 2 summarises the principal results of X-ray diffraction studies on ionic acylium salts (I).

As can be seen from Fig. 1 and Table 2, there is a chemical bond between the cation and the anion in the acylium salts. The C(2)–C(1)–O fragment has a linear structure corresponding to the *sp* hybridisation of the carbonyl carbon atom C(1). Thus the C(2)–C(1)–O angles are in all cases close to 180° and the C(1)–O bonds (~1.11 Å) are appreciably shorter than the $C_{sp^2}=O$ bond (1.20 Å for ketones and 1.17 Å for haloacyls[50,51]); the C(1)–O bonds in acylium cations are actually somewhat shorter than in the CO molecule (1.128 Å [45]) (Table 2).

The structure of the anionic fragment is close to a tetrahedron ($AlCl_4^{\ominus}$ and $GaCl_4^{\ominus}$) or an octahedron ($SbX_6^{\ominus}$) and the Al–Cl, Ga–Cl, and Sb–Cl bond length are close to the corresponding values for inorganic salts.

It follows from Table 2 that the C(1)–O bond lengths in various acylium salts are similar (~1.11 Å). On the other hand, the C(1)–C(2) bond length depends to a considerable extent on the nature of the group in which the C(2) atom is incorporated. For R = alkyl, the bond length is in the range 1.44–1.45 Å [the unduly short length quoted for the C(1)–C(2) bond in the compound $CH_3CO^{\oplus}SbF_6^{\ominus}$ is doubtful]. The closeness of these values to the $C_{sp^3}-C_{sp}$ bond length in the isoelectronic $CH_3C{\equiv}CH$ and $CH_3-C{\equiv}N$ molecules (1.46 Å [43,50]) does not provide grounds for the assertion that the resonance ketene form (A''') makes a contribution (see Scheme 3) to the structure of acylium salts in the crystal.[43,47,48] This conclusion is wholly confirmed by the ideal tetrahedral geometry at the C(2) atom.

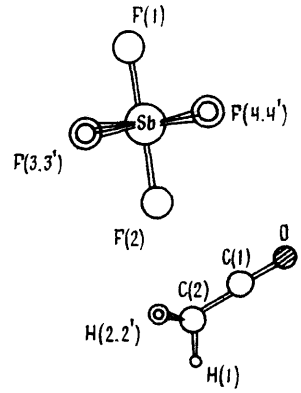
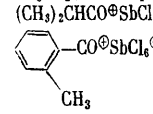
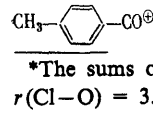


Figure 1. The structure of acetylium hexafluoroantimonate $CH_3CO^{\oplus}SbF_6^{\ominus}$.

Table 2. Geometrical parameters of the acylium salts $RCO^{\oplus}MX^{\ominus}_{n+1}$ (I) according to X-ray diffraction data.

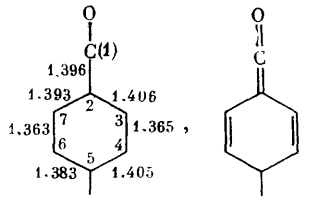
$RCO^{\oplus}MX^{\ominus}_{n+1}$	Bond lengths, Å		Minimum distances between non-bonded atoms*, Å			C(2)–C(1)–O angle, deg	Refs.
	C(1)–O	C(1)–C(2)	Cl–C(1)	Cl–O	Cl–C(2)H$_3$		
$CH_3CO^{\oplus}SbCl_6^{\ominus}$	1.109	1.452	3.34	3.58	3.55	180.0	[43,44]
$CH_3CO^{\oplus}AlCl_4^{\ominus}$	1.11 *	1.45 *	3.33	3.43	3.49	179.8	[43]
$CH_3CO^{\oplus}SbF_6^{\ominus}$	1.108	1.385				177.2	[45,46]
$CH_3CH_2CO^{\oplus}GaCl_4^{\ominus}$	1.099	1.435	3.42	3.43	3.51	177.7	[47]
$(CH_3)_2CHCO^{\oplus}SbCl_6^{\ominus}$	1.116	1.439	3.27	3.43	3.58	175.7	[47,48]
	1.111	1.387	3.31	3.42		178.7	[49]
	1.097	1.396	3.29	3.35		179.4	[41]

*The sums of the van der Waals radii are $r(C_{sp^2}-Cl)$ = 3.4 Å, $r(Cl-O)$ = 3.2 Å, and $r(C_{sp^3}-Cl)$ = 3.8 Å.

**Only the C(2)–O distance has been determined (2.56 Å). However, taking into account the constancy of the C(1)–O distances (1.11 Å), the C(2)–C(1) bond length was assumed to be 1.45 Å.[43]

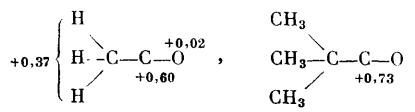
The structural data for the aryl cations $ArCO^{\oplus}$ leads to the opposite conclusion. It follows from Table 2 that in this case the C(1)–C(2) bond is somewhat shorter (~1.39 Å) than the $C_{sp^2}-C_{sp}$

bond in the isoelectronic PhC≡N (1.42 Å [50,51]). At the same time a shortening of the C(3)–C(4) and C(6)–C(7) bonds in benzene rings has been observed, which indicates a contribution by ketene-like structures:



X-Ray diffraction data also yield valuable information about the distribution of electron density in acylium cations. Thus comparison of the distances in the intramolecular contacts between non-bonded atoms shows that the C(1)–Cl and CH_3–Cl distances are almost always smaller than the sum of the corresponding van der Waals radii. On the other hand, the Cl–O distances exceed the sum of the van der Waals radii of Cl and O (Table 2). Thus structural data show that the positive charge in the cation $CH_3CO^{\oplus}$ is located mainly on the C(1) atom and the hydrogen atoms at C(2), which confirms the importance of the resonance forms (A″) and (A‴) [but not (A′)] in the crystal structures of acylium salts (see Scheme 3).

This conclusion agrees with the results of quantum-chemical calculations of the distribution of electron density in the cations $CH_3CO^{\oplus}$ and $(CH_3)_2CHCO^{\oplus}$ by the *ab initio* method,[33] whose results are presented below:



Calculation shows that the positive charge in the acylium cation is concentrated mainly on the carbon atom, while the oxygen atom is almost electrically neutral and the hydrogen atoms acquire an appreciable positive charge, shielding the C(2) atom.

It is noteworthy that the quantum-chemical calculations for the $RCO^{\oplus}$ structure (R = alkyl)[33] agree well with experimental bond lengths and angles quoted above (Table 2) for the $CH_3CO^{\oplus}$ cation. Another distribution of electron density in the $CH_3CO^{\oplus}$ ion, obtained on the basis of Boer's results,[45] appears less likely, since, according to these data, the charge on the hydrogen atoms (+0.07) in $CH_3CO^{\oplus}$ is close to the charge on the hydrogen atoms in ethane, which conflicts with the results of other studies indicating an appreciable deshielding of these atoms.

2. The structure of the donor–acceptor complexes RC(X)=O → MX_n

Fig. 2 illustrates the structure of the donor–acceptor complex and Table 3 lists the principal geometrical parameters of the type (II) complexes investigated.

X-Ray diffraction data demonstrate that the Lewis acid is coordinated to the electron pair of the oxygen atom. This is confirmed unambiguously by the presence of the M–O bonds. Thus the Al–O bond lengths in the type (II) complexes (1.820–1.847 Å) exceed only slightly the Al–O bond lengths in stable compounds such as aluminosilicates (1.79 Å). On the other hand, the Sb–O bonds (2.3–2.4 Å) in complexes (III) are significantly longer than, for example, in the complexes $Cl_3P{=}O \rightarrow SbCl_5$ (2.17 Å [52]) and $Me_3P{=}O \rightarrow SbCl_5$ (1.94 Å [53]), which indicates a lower stability of the complexes of acyl halides with acids such as $SbCl_5$ compared with $AlCl_3$.

Complex formation via the oxygen atom leads to the lengthening of the C(1)–O bond (1.21–1.24 Å) compared with the length 1.17 Å in the non-coordinated RCOX,[50] the C(1)–O bond lengths [as well as the C(1)–Cl bond lengths] in the adducts being distinguished by a marked constancy, which apparently indicates a similar strength of the C(1)–O bonds in type (II) complexes.

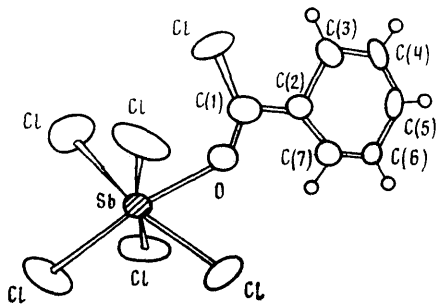


Figure 2. The structure of a type (II) coordination complex: $PhC(Cl){=}O \rightarrow SbCl_5$.

The C(1)–C(2) bond length in the CH_3CH_2–C(Cl)=O → $AlCl_3$ is close to the length of the classical C_{sp^3}–C_{sp^2} bond (1.49 Å [54]), while the Ar–C(1) bonds in ArC(X)=O → MX_n are appreciably shortened compared with C_{sp^2}–C_{sp^2} (1.47 Å [50]).

An important feature of the geometry of the donor–acceptor complexes is the appreciable increase of the M–O–C(1) angles (142–176°) compared with the value 120° characteristic of the sp^2-hybridised oxygen atom. Such a marked distortion of the angles has been attributed[41] to the steric effects observed in the packing of the crystal. On the other hand, the deformations of the angles at the carbonyl carbon atom C(1) are small. The $OAlCl_3$ and $OSbCl_5$ fragments have the geometries of a somewhat distorted tetrahedron and octahedron respectively.

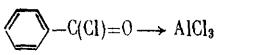
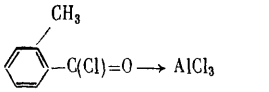
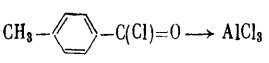
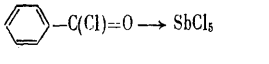
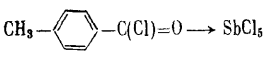
Thus the X-ray diffraction method yields valuable information about the structures of complexes (I) and (II) in the crystalline state.

V. Spectroscopic studies on the structures of the complexes RCOX.MX_n

1. ^{81}Br NQR study of the complex AcBr.$AlBr_3$

A single example of the application of the ^{81}Br NQR method to the study of the structures of complexes of the type RCOX.MX_n, namely AcBr.$AlBr_3$ at 77 K, has been described.[55] The spectrum of this complex lies in the same frequency range as that of the salt $KAlBr_4$.[56] Frequencies in the region corresponding to the vibrations of the C–Br bonds are not then observed at all, so that the presence of free AcBr and of the coordination complex $CH_3C(Br){=}O \rightarrow AlBr_3$ can be fully excluded. Thus at 77 K the complex AcBr.$AlBr_3$ consists of the ionic acetylium salt $Ac^{\oplus}AlBr_4^{\ominus}$. It follows from the multiplicity and relative intensities of the lines

Table 3. Geometrical parameters of the donor–acceptor complexes $RC(X)=O \rightarrow MX_n$ (II) according to X-ray diffraction data.

$R-C(X)=O \rightarrow MX_n$ (II)	Bond lengths*, Å			Angles, deg				Refs.
	M–O	C(1)–O	C(1)–C(2)	M–O–C(1)	O–C(1)–C(2)	O–C(1)–Cl	C(2)–C(1)–Cl	
$CH_3CH_2C(Cl)=O \longrightarrow AlCl_3$	1.847	1.221	1.488	141.6	124.5	119.1	116.1	[37]
	1.820	1.226	1.420					[38]
	1.824	1.235	1.442	146.2	124.3	117.0	118.7	[39]
	1.828	1.235	1.432	144.6	122.4	118.5	119.1	[39]
	2.317	1.236	1.453	145.9	121.0	121.1	117.9	[40]
	2.253	1.220	1.434	146.6	122.3	119.4	118.3	[41]
$(CH_2C(Cl)=O \longrightarrow SbCl_5)_2$	2.428	1.211	1.508	175.8	123.9	123.1	113.0	[42]

* The C–Cl bond lengths are similar for all the complexes, amounting to 1.71–1.72 Å.

that the unit cell contains two crystallographically independent $AlBr_4^{\ominus}$ anions. Above 77 K, the NQR spectrum cannot be observed, probably owing to the intense molecular movements in the crystal.

The same complex, obtained in an excess of CH_2Br_2, retains in the solid state its acylium structure, which differs, however, from the structure of the complex obtained in the absence of CH_2Br_2. The difference consists in the fact that, in the complex obtained in CH_2Br_2, the anion $AlBr_4^{\ominus}$ is additionally coordinated to the CH_2Br_2 molecule, i.e. the complex formed has the structure $Ac^{\oplus}[AlBr_4 \rightarrow CH_2Br_2]^{\ominus}$. Such interaction of the anion with a solvent molecule is manifested by a hypsochromic shift of the four lines corresponding to $AlBr_4^{\ominus}$ and by a decrease in the vibration frequency of the C–Br bond of methylene bromide.

However, the most extensive information about the structure of the complexes $RCOX.MX_n$ in the solid state and even more so in solution has been obtained by NMR and IR spectroscopy.

2. Identification of acylium salts by vibrational spectroscopy

As already mentioned, complex formation has an appreciable influence on the length of the C=O bond in RCOX, whose multiplicity increases in the acylium salts (I) and decreases in the donor–acceptor complexes (II). Accordingly, the formation of the acylium salt (I) is accompanied by a hypsochromic shift of the stretching vibration frequencies [ν(CO)] in RCOX, while the formation of complex (II) is accompanied by a bathochromic shift of this frequency.

Acylium salts can be clearly identified from the manifestation of an intense absorption in the frequency range 2200–2300 cm^{-1} corresponding to the stretching vibrations of the $[C=O]^{\oplus}$ bond (Table 4) and the vibrations of the M–X bonds in the anions $MX_4^{\ominus}$ or $MX_6^{\ominus}$.[1,5,7,17] This is accompanied by the disappearance of the stretching vibration frequencies of C=O [ν(CO) = 1750–1850 cm^{-1}] and C–X of the non-coordinated RCOX, while the stretching vibration frequencies of the C–H and C–C bonds are altered.

Although the appearance of a new high-frequency absorption undoubtedly indicates the formation of complexes (I), a complete interpretation of the absorption bands in the above region encountered serious difficulties for a long time. The point is that not one but two frequenices are very frequently observed in the range 2200–2300 cm^{-1} (Table 4).

In order to account for the presence of two frequencies, at ~2300 and ~2200 cm^{-1}, in the $AcCl.AlCl_3$ system, Cook[63,68] suggested that, apart from the acylium salt, complex (IV) is present (Scheme 1). In this complex the electron-deficient $CH_3CO^{\oplus}$ cation is additionally coordinated to the $AlCl_3$ molecule:

$$\underset{(I)}{CH_3CO^{\oplus}AlCl_4^{\ominus}} \quad \underset{(IV)}{[CH_3C^{\oplus}=O \rightarrow AlCl_3]Cl^{\ominus}}$$

$\nu(CO) = 2203\ cm^{-1}$, $\nu(CO) = 2307\ cm^{-1}$.

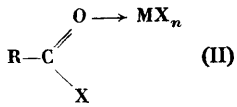
In contrast to Cassimatis's assignment,[62,66] Cook assigned to the $CH_3CO^{\oplus}$ cation the vibration with frequency ν(CO) = 2203 cm^{-1}, while frequency ν(CO) = 2307 cm^{-1} was assigned to complex (IV).[63,68]

Assuming that the formation of complex (IV), via the complex formation reaction between the electron-deficient species $CH_3CO^{\oplus}$ and the Lewis acid, is unlikely, Cassimatis[62,66] proposed the existence in equilibrium with the acetylium salt of its resonance hybrid, the cationic form (A‴) predominating:

$$\underset{2200\ cm^{-1}}{CH_3CO^{\oplus}} \rightleftarrows \underbrace{\{\underset{(A')}{CH_3C{\equiv}O^{\oplus}} \longleftrightarrow \underset{(A'')}{CH_3C^{\oplus}=O} \longleftrightarrow \underset{(A''')}{CH_2=C=O\overset{H^{\oplus}}{\}}}}_{2300\ cm^{-1}}.$$

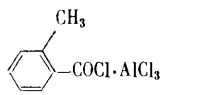
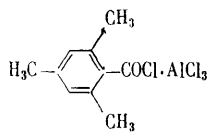
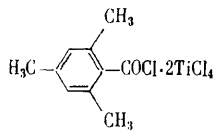
However, the hypothesis of the existence of two resonance structures as two individual complexes appears to be at least peculiar.

Table 4. Parameters of the IR spectra of certain



(II)

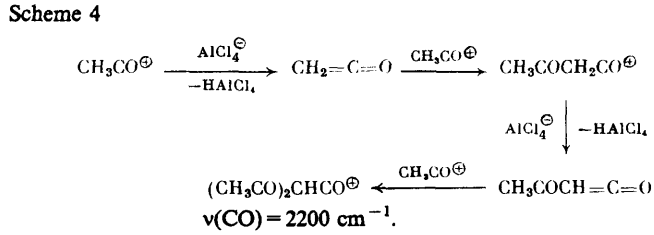
and $RCO^{\oplus}MX_{n+1}^{\ominus}$ (I) systems without a solvent.

$RCOX \cdot MX_n$	ν(CO), cm^{-1} (II)	ν(CO), cm^{-1} (I)	Refs.
$CH_3COF \cdot SbF_5$	1621 w; 1554 w	2294 s	[25]
$CH_3CH_2COF \cdot SbF_5$	1610 m	2290 s	[25, 57]
$(CH_3)_3CCOF \cdot SbF_5$	1570 m	2260 s	[27]
$PhCOF \cdot SbF_5$	1546 s; 1531 m	2212 s	[25, 57]
$PhCH_2COF \cdot SbF_5$	1599 m; 1516 m	2279 s	[27]
$SbF_5 \cdot FOC(CH_2)_3COF \cdot SbF_5$	—	2290 s	[58]
$CH_3COF \cdot AsF_5$	1620 w; 1558 w	2302 s	[25]
$CH_3COCl \cdot SbCl_5$	1709 m; 1587 w	2283 s	[25, 59]
$PhCOCl \cdot SbCl_5$	1656 s; 1575 s	2215 w	[25]
$CH_3COF \cdot BF_3$	1619 m; 1560 w	2299 s	[60, 61]
$CH_3COCl \cdot AlCl_3$	1639 m; 1560 w	2305 s	[31]
$CH_3COCl \cdot AlCl_3$	1633 s; 1560 s	2300 s; 2200 s	[62]
$CH_3COCl \cdot AlCl_3$	1637 s; 1567 s	2307 s; 2203 s	[39, 63, 64]
$PhCOCl \cdot AlCl_3$	1585 m; 1525 m	–	[23, 65]
	1602 m; 1525 m	2200 s	[23]
	1535 m	2190 s	[31]
$CH_3COBr \cdot AlBr_3$	1630 s; 1555 s	2300 s; 2200 w	[66]
$PhCOCl \cdot AlBr_3$	1540 s	—	[67]
$CH_3COCl \cdot GaCl_3$	1616 m; 1540 w	2300 s	[68]
$CH_3COCl \cdot TiCl_4$	1763 m*; 1620 s	–	[67, 69]
$PhCOCl \cdot TiCl_4$	1615 s; 1553 s	–	[23, 67]
	–	2170 s	[23, 67]

*This frequency is discussed in the text.

The controversial problem of the nature of the complex responsible for the appearance of the second absorption band in the range 2200–2300 cm^{-1} was successfully solved by Germain et al.[70,71] after it had been shown that, together with the acetylium salt $CH_3CO^{\oplus}AlCl_4^{\ominus}$ [ν(CO) = 2300 cm^{-1}], the product of the self-acylation of this salt—diacetylacetylium tetrachloroaluminate $(CH_3CO)_2CHCO^{\oplus}AlCl_4^{\ominus}$ [ν(CO) = 2200 cm^{-1}]—can be formed in the AcCl–$AlCl_3$ system. This process, which proceeds via the formation of the ketene form is illustrated in Scheme 4.

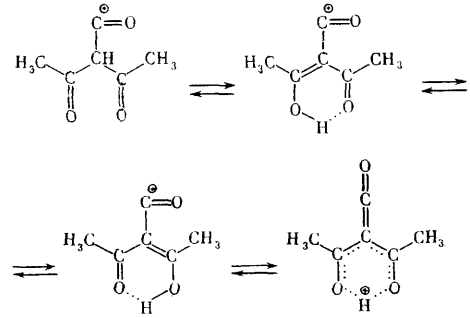
Scheme 4



ν(CO) = 2200 cm^{-1}.

The bathochromic shift of the absorption band of the $[C=O]^{\oplus}$ bond [ν(CO)] in the doubly acylated acylium salts relative to the corresponding bond in RCO^+ (R = alkyl) is quite reasonable if one takes into account the fact that in the given instance one should expect an appreciable contribution by the ketene-like limiting structure in which the $[C=O]^+$ bond has been lengthened:

Scheme 5



ν(CO) = 2200 cm^{-1}.

Both complexes, $CH_3CO^{\oplus}AlX_4^{\ominus}$ and $(CH_3CO)_2CHCO^{\oplus}AlX_4^{\ominus}$, were isolated in a pure form and were characterised. The self-acylation of the acetylium ion depends on the conditions under which the complexes are prepared, the nucleophilicity of the anion (thus self-acylation is not observed in the case of the weakly nucleophilic anion $SbF_6^{\ominus}$), and on the nature of R in $RCO^{\oplus}$ ($ArCO^{\oplus}$ does not form diacylated salts). The presence of the second frequency in the range 2200–2300 cm^{-1} is therefore not always observed (Table 4).

It follows from the foregoing that at the present time the IR spectra make it possible to detect reliably the formation of the ionic complexes (I). Table 5 lists the observed IR frequencies of the $CH_3CO^{\oplus}$ and $CD_3CO^{\oplus}$ ions and their assignments.[62]

Table 5. The assignments of the frequencies in the IR spectra of the cations $CH_3CO^{\oplus}$ and $CD_3CO^{\oplus}$.[62]

Frequency, cm^{-1}		Assignment
$CH_3CO^{\oplus}$	$CD_3CO^{\oplus}$	
2940 s	2209 s	ν(CH_3) (asym.)
2870 s	2049 s	ν(CH_3) (sym.)
2295 s	2297 s	ν(C=O)
1360 w	980 w	δ(CH_3) (asym.)
1319 s	1056 s	δ(CH_3) (sym.)
950 s	834 s	ν(C–C)
390 m	370 m	ν(C–C)

Analysis of the data in Table 4 shows that, with increase in the positive inductive effect of the group R in $RCO^{\oplus}$, which diminishes the charge on the carbonyl carbon atom, a bathochromic shift of the ν(CO) frequency is observed. For example, a bathochromic shift is

observed with increase in the number of methyl groups at the α-carbon atom:

	$(CH_3)_3CCO^{\oplus}$	$(CH_3)_2CHCO^{\oplus}$	$CH_3CH_2CO^{\oplus}$
ν(CO), cm^{-1}	2260	2270	2290

increase of the $+I$ effect of the group R

The factors promoting the stabilisation of the ketene form (A‴) also reduce the C–O bond order and hence lead to a bathochromic shift of the absorption band of this bond. Thus the lower frequencies [ν(CO) $\simeq$ 2200 cm^{-1}] for the cation $(CH_3CO)_2CHCO^{\oplus}$ or the cations $ArCO^{\oplus}$ compared with aliphatic acylium ions (Table 4) are due to the significantly greater contribution of the ketene structure.

3. Identification of donor–acceptor complexes by vibrational spectroscopy

As already mentioned, the formation of the $C=O\rightarrow MX_n$ donor–acceptor bond is accompanied by a bathochromic shift of the carbonyl group frequency (from 1750–1850 to 1560–1640 cm^{-1}).[1,5,7,17,18]

However, as can be seen from Table 4, not one but two frequencies are often observed in the range 1560–1640 cm^{-1}. The question of the assignment of these frequencies has been widely discussed in the literature but the situation is still not entirely clear. Different workers attribute different frequencies to the $\nu(C=O\rightarrow)$ vibration for the same complexes $RC(X)=O\rightarrow MX_n$: in the range 1560–1570 cm^{-1} according to Susz and Wuhrmann[31] and Cassimatis and Bonnin[62] or in the range 1620–1640 cm^{-1} according to the assignment by other workers.[43,63,64,68] Thus, in a study of the $AcCl.AlCl_3$ system in the solid state, Susz[31] observed in the IR spectrum, together with the intense frequency due to the acylium ion, a weak frequency at 1540 cm^{-1} and a very weak frequency at 1640 cm^{-1}. He suggested that the former refers to $\nu(C=O\rightarrow)$ for a type (II) donor–acceptor complex and the latter is caused by the formation of the product of the decomposition of the acylium salt—a type (V) "Illary complex" $CH_2=C(Cl)OAlCl_2$ and represents the stretching vibration frequency of the C=C bonds. However, the synthesis of the complex $AcCl.AlCl_3$ both at −15 °C and at 27 °C led to a product with the empirical formula $C_2H_3OAlCl_4$, i.e. the formation of an "Illary complex" was not confirmed and the problem of the assignment of the 1640 and 1560 cm^{-1} frequencies remained unsolved.

Another system investigated, namely $AcCl.TiCl_4$, did not contain acylium salts and the IR spectrum exhibited two absorption bands at 1620 and 1763 cm^{-1} which have undergone a bathochromic shift relative to ν(CO) for the non-coordinated carbonyl group in AcCl.[67,69]

Calculation of the force constants on the assumption that the 1620 cm^{-1} frequency is due to the $C=O\rightarrow TiCl_4$ coordinate bond led to more reasonable values than for the assignment of the 1763 cm^{-1} frequency to this bond.[69] The authors hypothesis that the 1763 cm^{-1} frequency is associated with the formation of a type (III) coordination complex via the chlorine atom appears to be unjustified, because the formation of such a complex should have been accompanied by a hypsochromic shift of the carbonyl frequency.

Susz[23,67] attributed the ν(CO) frequency in the range 1530 to 1560 cm^{-1} to the aromatic type (II) complexes $ArC(X)=O\rightarrow MX_n$ (MX_n = $AlCl_3$, $TiCl_4$, SbF_5), while in another study[72] frequencies in the range 1620–1630 cm^{-1} were assigned to ν(CO) for the weaker complexes $ArC(X)=O\rightarrow TiCl_4$ and it was noted that $SbCl_5$, being a stronger acceptor, induces a shift of the carbonyl frequency of the initial ArCOX by 210–220 cm^{-1}, while $TiCl_4$ gives rise to a shift of 140–150 cm^{-1}.

The identification of complexes (II) from the C–Hal bond vibrations presents an even greater difficulty. Furthermore, it is still not clear how ν(C–Cl) changes on coordination of MX_n to oxygen.

In most studies the appearance of a new ν(C–X) frequency on coordination of MX_n to oxygen is not reported at all. Cook[63] suggested that such coordination leads to the loosening of the C–Cl bond and to a pronounced bathochromic shift of this frequency to a region inaccessible to observation by IR spectroscopy. On the other hand, Jones and Wood[65] suggest that the force constant of the C–Cl bond increases on coordination of MX_n to oxygen and that ν(C–Cl) undergoes an appreciable hypsochromic shift. These workers attributed a value of 945 cm^{-1} to the ν(C–Cl) frequency in the spectrum of the complex $PhC(Cl)=O\rightarrow AlCl_3$ [for non-coordinated PhCOCl, ν(C–Cl) = 877 cm^{-1}].

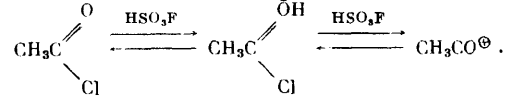
Cassimatis and Bonnin suggested[62] that the C–Cl bond in complexes (II) changes very insignificantly and attributed the low intensity vibration at 605 cm^{-1} to ν(C–Cl) for the complex $CH_3C(Cl)=O\rightarrow AlCl_3$ [ν(C–Cl) = 593 cm^{-1} for AcCl]. This second hypothesis that the C–Cl frequency changes only slightly (and that its intensity probably diminishes) appears more probable, since it agrees well with X-ray diffraction data indicating a small change in the C–Cl bond length on coordination to the oxygen atom.

Thus the disappearance of the frequency of the carbonyl group of the acyl halide and the appearance of a new frequency in the range 1530–1630 cm^{-1} indicate the formation of a donor–acceptor complex. However, a reliable assignment of the observed frequencies is as a rule extremely difficult.

One cannot rule out the possibility that, in the case of the acetyl complexes, the appearance of frequencies in the region 1530–1630 cm^{-1} of the IR spectrum may be due to the formation of the cation of protonated acetic acid $CH_3C(OH)_2^{\oplus}$ in the presence of traces of moisture.[73] This possibility is confirmed by the appearance of frequencies in the range 1550–1660 cm^{-1} after the addition of water to acylium salts.[58,74] The $RCOX.MX_n$ systems should therefore be studied in the complete absence of traces of moisture.

It is also necessary to take into account the fact that the salt optical components (especially NaCl and KBr glass) used to record IR spectra are not indifferent to the $RCOX.MX_n$ complexes. This probably explains the partial discrepancies between the IR spectra of the same systems in different publications and the at first sight paradoxical data showing that the crystals of individual complexes (I) exhibit in their IR spectra the presence, apart from their own frequencies, also of those complexes (II).[43]

This disadvantage in the study of the $RCOX.MX_n$ systems can be avoided by using Raman spectroscopy, which permits measurements in sealed glass tubes. Unfortunately Raman spectroscopy has not yet come to be widely used for the study of the $RCOX.MX_n$ complexes and similar systems. As examples of its employment, one may only quote isolated studies.[59,75] Thus, in a study of the spectra of solutions of AcCl in strong Brønsted acids (FSO_3H, $ClSO_3H$, etc.), Corriu et al.[75] showed that equilibrium involving the free AcCl, its protonated form, and the acetyl cation is observed in such systems:



The frequency ν(CO) of the cation $CH_3CO^{\oplus}$ in the Raman spectrum is 2309 cm^{-1}, while that of $CH_3C(Cl)=OH^{\oplus}$ is 1420 cm^{-1}, which indicates a stronger binding of the acyl halide to the proton compared with MX_n.

4. ^{1}H NMR study of the RCOX.MX_n systems

NMR spectroscopy has found extensive applications in the study of the RCOX.MX_n systems in solutions. This method makes it possible to identify complexes (I) and (II), to determine their content in the mixture, and to obtain information about the nature of the distribution of charges in complexes (I) and (II) in solutions of different kinds and about the interconversions between them.[1,5,7,17]

The ^{1}H NMR spectra of these systems were first described by Olah and co-workers.[25,27] The spectra of the AcF.SbF_5 systems in SO_2 or HF contain, apart from the signal due to the initial AcF (doublet with $J_{H-F} \simeq 7$ Hz), two new singlets located in a weaker field. The signal with δ_{CH_3} = 4.08 p.p.m. (singlet) has been assigned to the acetylium salt $CH_3CO^{\oplus}SbF_6^{\ominus}$ (I), while the singlet with the chemical shift δ_{CH_3} = 2.94 p.p.m. was assigned to the coordination complex $CH_3C(F)=O \rightarrow SbF_5$ (II).

The absence of splitting by the ^{19}F nucleus of the signal of the CH_3 group in complex (II), which is observed in the initial AcF, indicates, according to the authors,[25] the existence of the dynamic equilibrium

$$CH_3CO^{\oplus}SbF_6^{\ominus} \underset{SO_2}{\rightleftharpoons} CH_3C(F)=O\rightarrow SbF_5$$

(I) (II)

δ_{CH_3}=4.08 p.p.m., δ_{CH_3}=2.94 p.p.m.

The ^{1}H NMR spectroscopic data for complexes (I) and (II) are presented in Table 6. It follows from these results that the signals of the β-hydrogen atoms (here and henceforth this term is given to the hydrogen atoms attached to the carbon atom which is linked to the carbonyl group) in the salts $RCO^{\oplus}MX_{n+1}^{\ominus}$ (I) (R = alkyl, MX_{n+1} = $SbF_6^{\ominus}$, $BF_4^{\ominus}$, $SbCl_6^{\ominus}$, $AlCl_4^{\ominus}$, $SO_3F^{\ominus}$) lie in the range 4.0–4.5 p.p.m. relative to TMS (the chemical shift δ = 3.9 to 4.2 p.p.m. is characteristic of R = CH_3). The resonance of the β-protons in such a weak field indicates a high acidity and hence the location of the positive charge in the acylium salts in solution mainly on the carbonyl carbon atom, as has been observed for the crystalline state.[17] The chemical shifts of the β-protons in the range 2.9–3.6 p.p.m., i.e. in a higher field, are characteristic of complexes (II).

The chemical shifts of the β-protons in the salt $CH_3CO^{\oplus}SbF_6^{\ominus}$ in solution in CH_3NO_2 and $PhNO_2$ have been observed in a higher field than for the solutions in HF or SO_2. Furthermore, in solutions in CH_3NO_2 and $PhNO_2$ there is a sharp rise in the content of complexes (II).[11] In view of the very high regioselectivity of *para*-substitution on acylation of alkylbenzenes by the RCOX.SbF_5 systems (in nitromethane[11] or sulpholan[57]), it was concluded that there are no free ions in such solvents and only close ion pairs are present.

As regards the differences between the chemical shifts for acylium cations with different anions and in different solvents, it is not useful to discuss them because of the low accuracy of the chemical shifts quoted in the literature due to the difficulty of selecting an internal standard for such reactive complexes. As a rule, the ^{1}H NMR spectra quoted in the literature have been recorded using external standards.

In the identification of the donor–acceptor complexes (II) by the ^{1}H NMR method, there are serious complications. Thus it has been found that, in "super acid" media carboxylic acids also form two types of complexes: a protonated acid (δ_{CH_3} = 3.2 p.p.m.) and an acetylium salt (δ_{CH_3} = 4.35 p.p.m.), the chemical shift δ_{CH_3} for the protonated acid being close to those adopted for type (II) complexes (Table 6).

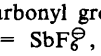
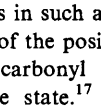
Scheme 6

$$CH_3C(=O)OH \underset{-60^\circ C}{\overset{H^{\oplus}}{\rightleftharpoons}} CH_3C(OH)_2^{\oplus} \underset{-30-0\ ^\circ C}{\overset{-H_2O}{\rightleftharpoons}} CH_3CO^{\oplus}$$

δ_{CH_3}=3.2 p.p.m., δ_{CH_3}=4.35 p.p.m.,

δ_{O-H}=12.4, 13.0 p.p.m.

Table 6. Parameters of the ^{1}H NMR spectra of the acylium salts and the coordination complexes (the chemical shifts are quoted relative to TMS).

RCOX.MX_n system	Solvent	δ, p.p.m.				Refs.
		$RCO^{\oplus}MX_{n+1}^{\ominus}$		$RC(=O\rightarrow MX_n)X$		
		β-H	γ-H	β-H	γ-H	
$CH_3COF\cdot SbF_5$	SO_2	4.1	–	2.9	–	[25]
$CH_3COF\cdot SbF_5$	CH_3NO_2	3.1	–	2.6 *1	–	[11]
$CH_3CH_2COF\cdot SbF_5$	SO_2	4.4	2.1	3.2	1.6	[25, 57]
$CH_3CH_2COF\cdot SbF_5$	HF	4.2	2.1	3.5	1.8	[25]
 $-COF\cdot SbF_5$	SO_2	4.5	2.6	Absent		[74]
$SbF_5\cdot COF(CH_2)_2COF\cdot SbF_5$	SO_2	4.6	3.7	3.7	4.6 *2	[58]
$SbF_5\cdot COF(CH_2)_3COF\cdot SbF_5$	SO_2	4.6	3.3	Absent		[58]
$(CH_3)_2CHCOF\cdot SbF_5$	SO_2	4.3	1.7	Absent *1		[27]
$PhCOF\cdot SbF_5$	SO_2	8.2–9.0		Absent		[25, 57]
	SO_2	7.3	8.9 8.6	Absent		[76]
$CH_3COF\cdot BF_3$	HF	4.2	–	3.0	–	[25]
$CH_3COCl\cdot AlCl_3$	CH_3NO_2	Absent		2.9 *1	–	[77]
$CH_3COCl\cdot SbCl_5$	$PhNO_2$	4.0	–	3.3 *1	–	[11]
$CH_3COCl\cdot AlCl_3$	$ClCH_2CH_2Cl$	Absent		3.4 *1	–	[77]
$CH_3COCl\cdot AlCl_3$	CH_2Cl_2	Absent		3.4	–	[78]
$CH_3COCl\cdot AlCl_3$	SO_2	4.2 *3	–	3.2	–	[79]
CH_3COOH	HSO_3F–SbF_5	4.4	–	3.2 *4	–	[80]

*1 The initial RCOX is also present in the solution.

*2 An ionic-coordination complex is formed.

*3 A different interpretation of the signals was given by Brownstein and Glavincevsky.[79]

*4 The protonated acid $CH_3C(OH)_2^{\oplus}$ is formed.

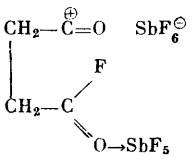
On this basis, Olah[7,58,80] revised his previous view concerning the presence of complexes (I) and (II) in the RCOF.SbF_5 systems in solutions in HF or SO_2 and assigned the ^{1}H NMR signal observed

in a strong field not to complex (II) but to the protonated acids $RC(OH)_2^{\oplus}$ formed as a result of the partial hydrolysis of ionic complexes (I). The fact that the addition of water to solutions of the $RCOF.SbF_5$ systems in SO_2 led to an increase in the high-field signal intensity and, conversely, that careful isolation from traces of moisture made it possible in certain instances to obtain for the first time solutions of the $RCOF.SbF_5$ systems in SO_2 containing only acylium salts $RCO^{\oplus}SbF_6^{\ominus}$ without any appreciable admixture of substances characterised by high-field signals (2.9–3.5 p.p.m.) constituted important evidence in support of the above hypothesis[57,58,74,76] (Table 6).

The presence or absence of signals due to the OH groups of the protonated acid $RC(OH)_2^{\oplus}$ (12–13 p.p.m. relative to TMS) (see Scheme 6) can apparently serve as an important criterion for the reliable assignment of the signals due to the CH_3 group observed in the region of ~3 p.p.m. Unfortunately, however, due attention has not been devoted to this problem in the literature concerned with the ^1H NMR spectroscopy of the $RCOX.MX_n$ systems.

Thus a reliable identification of the donor–acceptor complexes (II) in solutions by the ^1H NMR method is possible only under conditions where moisture is completely excluded.

The $RCOF.SbF_5$ systems in SO_2 (R = aryl, cycloalkyl, etc.) and $SbF_5.FCO(CH_2)_nCOF.SbF_5$ systems with $n \geqslant 3$ constitute as a rule ionic complexes (I) $RCO^{\oplus}SbF_6^{\ominus}$ and $SbF_6^{\ominus}{}^{\oplus}CO-(CH_2)_n-CO^{\oplus}SbF_6^{\ominus}$ [58] (Table 6). It is of interest that the latter complexes with $n = 2$ have the structure of ionic-coordination complexes in solution in SO_2.



The mutual influence of the oxocarbenium group is responsible for the change in structure from that of the diacylium salt ($n \geqslant 3$) to that of the ionic-coordination complex ($n = 2$). This also probably explains the failure of attempts to synthesise the complexes of SbF_5 with malonic acid difluoride ($n = 1$).

Since solvents such as SO_2 and HF are relatively unsuitable for catalytic reactions,[11] the structure of the $RCOX.MX_n$ system in organic media of low polarities is of special interest.

As shown above, the $RCOX.SbX_5$ (X = Cl, F) systems have been most thoroughly investigated by the NMR method in solvents such as SO_2, HF, CH_3NO_2, $PhNO_2$, and sulpholan, while in weakly polar solvents such as CH_2Cl_2, $C_2H_4Cl_2$, and $CHCl_3$ their investigation is hindered by the poor solubility and high oxidising capacity of antimony(V) derivatives. The NMR data for the structures of these systems in weakly polar solutions are therefore lacking in the literature. On the other hand, the $RCOX.AlX_3$ systems have been studied in both polar and weakly polar organic solvents.

The only solvent in which the ionic salts $RCO^{\oplus}AlCl_4^{\ominus}$ with R = Alk can apparently exist is SO_2. The $AcCl.AlCl_3$ systems in solution in SO_2 have been investigated,[71,79] but the results of these studies do not agree fully and have been given the opposite interpretation in the two investigations.

French investigators[71] concentrated attention on demonstrating the formation of the complex $(CH_3CO)_2CHCO^{\oplus}AlCl_4^{\ominus}$ in the $AcCl.AlCl_3$ system containing an excess of the acid chloride and there is no doubt that this does happen. The chemical shifts δ_{CH_3} = 3.0 and 3.97 p.p.m. are quoted for the salts $(CH_3CO)_2CHCO^{\oplus}AlCl_4^{\ominus}$ and $CH_3CO^{\oplus}AlCl_4^{\ominus}$ respectively in SO_2 (with MS as the external standard). Unfortunately the above workers concentrated attention on cationic species without presenting any data concerning complexes (II). Their second communication[79] reports the presence in the $AcCl.AlCl_3$ system of two complexes with δ = 4.18 and 3.20 p.p.m. This study will be discussed below [see Section (V)].

In all other solvents except $SO_2(C_6H_5NO_2$, CH_3NO_2,[77] CH_2Cl_2,[63,78] $C_2H_4Cl_2$,[77] etc.), the $CH_3COCl.AlCl_3$ system, having an ionic structure in the solid state, exists exclusively as the coordination complex (II). Apart from spectroscopic data, Wilinsky and Kurland[78] also describe chemical tests confirming the foregoing. Although this evidence is in our view not absolute, the conclusion that only complexes (II) are present is incontrovertible.

Thus one may conclude that, on the whole, conditions for the stabilisation of the ionic salts $RCO^{\oplus}MX_{n+1}^{\ominus}$ in weakly polar organic solvents have not so far been found for the $RCOX.MX_n$ (1 : 1) systems. As regards the complexes $RCOX.AlX_3$ (X = Cl, Br), the formation of the ionic salts $RCO^{\oplus}AlX_4^{\ominus}$ has not been observed for them also in more highly ionising media. We may note that the problem of the stabilisation of acylium salts in organic solvents has a direct bearing on the creation of highly reactive electrophiles.

5. ^{13}C NMR study of the $RCOX.MX_n$ systems

Important information about the composition of the $RCOX.MX_n$ systems in solutions and about the nature of complexes (I) and (II) has been obtained with the aid of ^{13}C NMR spectra.

Firstly, the characteristic chemical shifts $\delta_{\alpha-^{13}C}$ and especially $\delta_{^{13}CO}$ make it possible to identify very reliably complexes of types (I) and (II) in solutions, since the relative changes in the chemical shifts are small on passing from one solvent to another and on replacing an internal standard by an external one, which is an advantage of this method over ^1H NMR spectroscopy. Secondly, the ^{13}C NMR spectra yield additional important information about the structure and distribution of charges in the acyl cations $RCO^{\oplus}$.[7,81]

The ^{13}C NMR spectrum of a solution of the salt $CH_3{}^{13}CO^{\oplus}SbF_6^{\ominus}$ (53% isotope enrichment) in liquid HF was first described by Olah,[27] who erroneously attributed the signal of the carbonyl carbon atom $\delta_{^{13}CO}$ = 194 p.p.m. observed in the spectrum of this solution (quartet with $^2J_{C-C-H}$ = 6.3 Hz) to the $CH_3CO^{\oplus}$ ion. The signal with δ = 152 p.p.m. observed in a strong field, also present in the spectrum of this solution (however, this was reported only in a later communication[82]), was assigned by the authors to the product of the hydrolysis of the acylium salt $RC(OH)_2^{\oplus}$. In a study of the ^{13}C NMR spectra of acetic and benzoic acids in sulphuric acid and oleum at different concentrations, Masiel and Traficante[83,84] also observed two signals in the region of $\delta_{^{13}CO} \simeq$ 190 and 150 p.p.m. Despite Olah's assignment,[27] the signals observed in a weak field were assigned, in conformity with the data of Deno et al.,[85] to the protonated acid ions $RC(OH)_2^{\oplus}$. The logic of the studies of Masiel and Traficante[83,84] and the data of Deno et al.[85] concerning the formation of acylium ions from carboxylic acids in an $H_2SO_4-SO_3$ medium with a high acidity seemingly led to the conclusion that the $\delta_{^{13}CO} \simeq$ 150 p.p.m. signal, arising in the presence of a high content of SO_3 in the H_2SO_4 solution, should be attributed to acylium ions. However, Olah's incorrect assignment prevented the authors from arriving at this conclusion. They were forced to conclude that acylium ions could not be observed and the mysterious signal with $\delta_{^{13}CO} \simeq$ 150 p.p.m. remained unidentified.

The study by Traficante and Masiel[84] forced Olah to return to the problem of the identification of the acylium ion. For this purpose, a joint ^{13}C and ^1H NMR study of RCOOH solutions in the "super-

acid" HSO_3F-SbF_5 was undertaken.[80,82] It was shown clearly that at $T < -30$ °C the above solvent contains only the protonated acid ions $RC(OH)_2^{\oplus}$ characterised by $\delta_{C^1H_3} = 3.2$ p.p.m. and $\delta_{^{13}CO} = 190$ p.p.m. [for $CH_3C(OH)_2^{\oplus}$]. At a higher temperature, the acylium ions with $\delta_{C^1H_3} = 4.2$ p.p.m. and $\delta_{^{13}CO} = 148$ p.p.m. are in equilibrium with the above species. These data agree with Traficante's observations and demonstrate that the unassigned signals in the region of 150 p.p.m. should be attributed to the acylium ions $RCO^{\oplus}$.

The validity of the assignment of the 150 p.p.m. chemical shift to the carbonyl carbon atom of acylium iodide was later demonstrated by solid-phase ^{13}C NMR for the ionic salt $CH_3CO^{\oplus}AlBr_4^{\ominus}$.[86]

Table 7 presents the principal characteristics of the ^{13}C NMR spectra of certain acylium salts and coordination complexes. It shows that the ^{13}CO NMR signal of the $RCO^{\oplus}$ cations is usually observed in the range 145–157 p.p.m. The upfield shift of this signal relative to RCOF or RCOOH (this was the cause of the initial confusion as regards the assignment) is due to the change in the hybridisation of the carbonyl carbon from the sp^2- to the *sp*-hybridised state (see Section IV).

Table 7. Parameters of the ^{13}C NMR spectra of the acylium salts and the coordination complexes (the chemical shifts are quoted in p.p.m. relative to TMS).

System	Solvent	Assignment	^{13}C NMR spectroscopic data			Refs.
			δ_{CO}	$^1J_{CCH}$	$\delta_{\alpha\text{-}C}$	
CH_3COF			163		18	[28]
$CH_3COF \cdot SbF_5$	SO_2-SbF_5	$CH_3CO^{\oplus}$	148	9.3	5 *1	[81]
$CH_3COF \cdot SbF_5$	SO_2 *2	$CH_3CO^{\oplus}$	152		7	[27, 28]
		$CH_3C(F)=O \rightarrow SbF_5$	194	6.0		
CH_3COOH	HSO_3F-SbF_5	$CH_3CO^{\oplus}$	150	9.3		[82–84]
		$CH_3C(OH)_2^{\oplus}$	192	6.5		
$PhCOF \cdot SbF_5$	HF or SO_2	$PhCO^{\oplus}$	154	–	88 *3	
		$PhC(F)=O \rightarrow SbF_5$	182	–		[82, 87]
$CH_3-C_6H_4-COF \cdot SbF_5$	SO_2	$CH_3-C_6H_4-CO^{\oplus}$	157	–	83 *4	[87]
PhCOOH	Et_2O		173			[82]
PhCOOH	HSO_3F-SbF_5	$PhCO^{\oplus}$	154			[81–84]
		$PhC(OH)_2^{\oplus}$	183			

*1 $^1J_{CH} = 147$ Hz for the cation $CH_3CO^{\oplus}$.

*2 In solution in HF, the values of δ_{CO} for the acetylium cation and the coordination complex are respectively 151 and 193 p.p.m.

*3 The ^{13}C chemical shifts for the *ortho*-, *meta*-, and *para*-, carbon atoms of the aromatic ring are respectively 141, 133, and 149 p.p.m.

*4 The ^{13}C chemical shifts for the *ortho*-, *meta*-, and *para*-, carbon atoms of the aromatic ring are respectively 140, 134, and 166 p.p.m.

The ^{13}C NMR spectra also indicate a significant shielding of the α-carbon atoms of the acylium ions $RCO^{\oplus}$. Thus, for R = alkyl, $\delta_{\alpha-^{13}C} \simeq 0$ (relative to TMS) despite the presence of the neighbouring carbonium ion centre, which agrees with the calculation of electron density based on the results of X-ray diffraction analysis, also indicating a pronounced shielding of the α-carbon atom (see Section III).

Similar values of $\delta_{^{13}CO} \simeq 154-157$ p.p.m. and a similar tendency towards the shielding of the C(1) atom of the aryl group ($\delta = 80-90$ p.p.m.) are characteristic of the $ArCO^{\oplus}$ cations. The appreciable contribution of ketene-like forms to the $ArCO^{\oplus}$ structure is indicated by the chemical shift of the carbon atoms in the 2- and 4-positions in the aryl group (see the footnote to Table 7). Evidently the latter are appreciably deshielded and the maximum positive charge is located on the atom attached to the electron-donating group.[84]

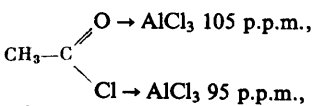
The formation of the type (II) complexes $RC(F)=O \rightarrow SbF_5$ (II) [or the protonated acids $RC(OH)_2^{\oplus}$] does not entail changes in hybridisation and the downfield shift of the signals observed in such cases ($\delta_{^{13}C-O\rightarrow} \simeq 190$ p.p.m.) is entirely logical and is associated with some displacement of electron density from the carbonyl group to the metal atom in MX_n.

The smaller positive charge on the carbonyl carbon atom in type (II) complexes induces a smaller deshielding (acidity) of the β-H atoms and hence a smaller shielding of the α-C atoms. As a result, the ^1H NMR signals of the β-protons in complexes (II) are located at a higher field (Table 6), while the signals of the corresponding α-^{13}C atoms are at a lower field compared with $RCO^{\oplus}$ ($\Delta\delta \simeq 20$ p.p.m.[81]).

6. Non-traditional types of treatment of the NMR spectra of the $RCOX.MX_n$ systems. Hypothesis of the existence of complexes other than $RCO^{\oplus}MX_{n+1}^{\ominus}$ and $RC(X)=O \rightarrow MN_x$

It follows from the foregoing that, in the course of the study of the complexes $RCOX.MX_n$, quite a few erroneous hypotheses were put forward and various contradictions arose, which have now been to a large extent resolved. In this Section we shall consider studies which reached conclusions different from those generally accepted or which we believe to be extremely doubtful on the basis of NMR spectra. Unfortunately, these investigations have not been assessed in the literature, with the exception of Olah's study[28] quoted in a review.[7]

Brownstein and Glavincevsky[79] investigated the complexes formed on interaction of AcCl with $AlCl_3$ in SO_2 by ^1H and ^{27}Al NMR at −24 to −54 °C. The reported composition of the system varies as a function of the reactant ratio. For the molar ratio $AcCl/AlCl_3 \geqslant 1$, a complex with $\delta_{^1H} = 4.18$ and $\delta_{^{27}Al} = 105$ p.p.m. is formed. The structure of a donor–acceptor complex (II) was assigned to it on the basis of the similarity of its ^{27}Al chemical shift to that observed by the same workers[88] for the complex $(CH_3)_2O \rightarrow AlCl_3$. The increase in the amount of $AlCl_3$ in the system to $AcCl:AlCl_3 = 1:(1.5-3)$ leads to the appearance in solution of yet another complex to which the authors[79] attribute the appearance of the second ^1H NMR signal with $\delta_{CH_3} = 3.2$ p.p.m. and the second signal in the ^{27}Al NMR spectrum with $\delta_{^{27}Al} = 95$ p.p.m. The structure of a donor–acceptor complex with additional coordination of one $AlCl_3$ molecule to the chlorine atom was assigned to this new complex:



3.2 p.p.m.

This conclusion is based on the closeness of the chemical shift of the new signal ($\delta_{^{27}Al} = 95$ p.p.m.) to the ^{27}Al chemical shift of the salt $Me_4N^{\oplus}AlCl_4^{\ominus}$.[88]

We believe that these conclusions[79] are erroneous. In our view, the additional coordination of an $AlCl_3$ molecule to the chlorine atom of the donor–acceptor complex (II) should lead to a downfield and not an upfield shift, of the kind observed by the above workers[79] for the signal due to the protons of the methyl group in the ^1H NMR spectrum. The appearance in the ^1H NMR spectrum of signals at a low field with increase in the acidity of the medium has in fact been observed by many workers (see, for example, Deno et al.[85]). A similar behaviour has been observed for the $AcX.nAlX_3$ systems in solution in CH_2X_2 with increase in the AlX_3 concentration.[86] We also think it unlikely that $AlCl_3$ should be coordinated to complex (II) and not to the free AcCl in the presence of free acid chloride in the system whose amount has been shown to be comparable,[79] even for an excess of $AlCl_3$, to the amount of complex (II). The fact that the assignments of the ^{27}Al spectra described by Brownstein and Glavincevsky[79] are actually the opposite of those put forward by other workers,[79,89–91] who assigned the chemical shift $\delta_{^{27}Al}$ = 93 p.p.m. (Δ = 300–500 Hz) to the coordinated $AlCl_3$ ($>C=O \rightarrow AlCl_3$) and the signal in the region of $\delta_{^{27}Al}$ = 102–107 p.p.m. (Δ = 10–30 Hz) to the anion $AlCl_4^{\ominus}$ is also somewhat perplexing.

Yet another study by the same workers[16] was devoted to the investigation of the $AcCl.SbCl_5$ system in solution in SO_2 by ^1H NMR. At −76 °C, the authors observed four signals with δ = 4.23, 3.02, 12.09, and 12.76 p.p.m. The first was attributed to a type (II) donor–acceptor complex, while the chemical shifts of 3.02, 12.09, and 12.76 p.p.m. were assigned to the salt $(CH_3CO)_2CHCO^{\oplus}SbCl_6^{\ominus}$. The authors assume that the last two signals correspond to the hydrogen atoms attached to a carbon or oxygen atom in the two tautomeric forms (see Scheme 5).

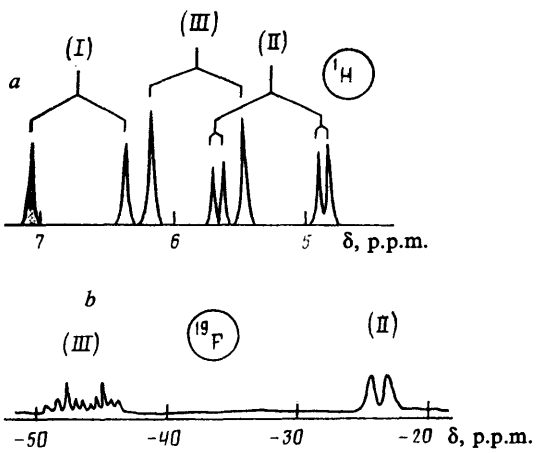
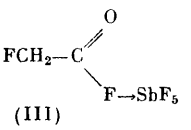


Figure 3. ^1H (*a*) and ^{19}F (*b*) NMR spectra of the $FCH_2COF.SbF_5$ system in SO_2 at −70 °C.

The validity of this interpretation[16] is open to serious doubt. Firstly, the observed ratios of the integral intensities (3 : 1 : 1) do not agree at all with the conclusion that $(CH_3CO)_2CHCO^{\oplus}SbCl_6^{\ominus}$ is present. Secondly, it had been shown earlier[92] that only a single signal with $\delta_{O...H}$ = 12.24 p.p.m., corresponding to the O-linked proton in the symmetrical ketene-like limiting structure, can be observed in a weak field in the ^1H NMR spectra of the salts $(CH_3CO)_2CHCO^{\oplus}MX_{n+1}^{\ominus}$ in solution in SO_2. On the other hand, the chemical shifts and the ratios of the intensities of the signals, attributed in the above study[16] to the diacetylacetylium salt, are fully consistent with the structure of the product of the hydrolysis of $CH_3CO^{\oplus}SbCl_6^{\ominus}$ — the protonated acid salt $CH_3C(OH)_2^{\oplus}SbCl_6^{\ominus}$.[74] The author's interpretation[16] of the ^1H NMR spectrum of a solution of the $CH_3COCl.SbCl_5$ system in SO_2 also appears erroneous.

In conclusion we shall consider Olah's study[28] in which the formation of a coordination complex via a halogen atom is reported:



(III)

In his study of FCH_2COF in the presence of an excess of SbF_5 in solution in SO_2 by the ^1H, ^{13}C, and ^{19}F NMR methods, Olah observed the presence of three complexes in equilibrium, to two of which the structure of the "classical" type (I) and (II) complexes was attributed, while the structure of the previously unknown complex (III) with the $RC(O)F \rightarrow SbF_5$ coordinate bond was assigned to the third complex (Fig. 3).

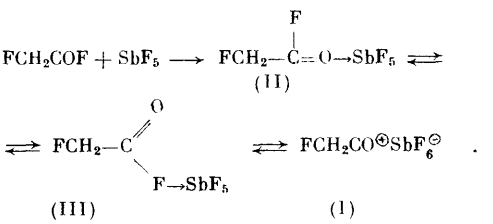


Table 8. The assignments of the ^{13}C, ^{19}F, and ^1H NMR chemical shifts of the complexes $FCH_2CO^{\oplus}SbF_6^{\ominus}$ (I), $FCH_2C(F)=O\rightarrow SbF_5$ (II), and $FCH_2C(=O)-F\rightarrow SbF_5$ (III).

Compound	Chemical shift δ, p.p.m.				
	CH_2F			COF	
	^1H	^{19}F	^{13}C	^{13}C	^{19}F
FCH_2COF	5.0	229.4	75.4	159.7	−22.7
$FCH_2C(F)=O\rightarrow SbF_5$ (II)	5.3	229.0	75.9	162.1	−23.8
$FCH_2C(=O)-F\rightarrow SbF_5$ (III)	5.9	232.4	77.1	180.3	−46.6
$FCH_2CO^{\oplus}SbF_6^{\ominus}$ (I)	6.8	234.6	75.4	145.1	–

Table 8 and Fig. 3 present the characteristics of the NMR spectra of the $FCH_2COF \rightarrow SbF_5$ system in solution in SO_2 at −70 to −30 °C. According to the authors,[28] the NMR spectra agree with the presence of equilibria involving complexes (I), (II), and (III). The formation of a complex with structure (III) is indicated by the following data: the intermediate position of the signal due to the FCH_2 group in the ^1H NMR spectrum relative to the corresponding signals of complexes (I) and (II), the virtual absence of changes in the ^{13}C and ^{19}F NMR spectra of this group, which makes it possible to rule out the coordination of SbF_5 to the fluorine atom of the FCH_2 group, the appreciable deshielding of the carbon atoms and

especially the fluorine atom of the COF group, and also the characteristic multiplicity (doublet of quintets) of the signal in the ^{19}F NMR spectrum of this group (Fig. 3 and Table 8). The molar ratios of complexes (II), (III), and (I) depend on temperature and are respectively 20:50:30 at −70 °C and 27:38:35 at −30 °C. Direct structural evidence is apparently necessary for the final confirmation of the possibility of the existence of type (III) complexes.

Although the formation of stable type (III) complexes containing the Hal → MX_n coordinate bond cannot be regarded as rigorously demonstrated, complexes of this type have been postulated[7,28] as intermediates in the conversion of donor–acceptor complexes (II) into ionic salts (I).

VI. Factors influencing the equilibrium between ionic and coordination complexes

Evidently the knowledge of factors influencing the equilibrium (I) ⇄ (II) (especially in solutions) and hence the reactivity of the RCOX.MX_n systems is very important. Unfortunately, there have been no systematic studies on this problem.

We shall consider briefly the few literature data concerning the influence of the nature of the groups R and Hal in RCOHal, the strength of the Lewis acid MX_n, the nature of the solvent, and temperature on the structures of the complexes formed and the equilibrium between them.

1. The influence of the groups R and Hal in RCOHal and of the strength of the Lewis acid

This problem has been examined in a review.[5] It follows from experimental data that the capacity of the halide RCOHal for the formation of ionic complexes diminishes in the sequence

$$F > Cl > Br > I .$$

The tendency to form ionic salts in the RCOX.MX_n systems depends still more significantly on the strength of the Lewis acid (MX_n). Thus strong Lewis acids form predominantly ionic salts, while weaker ones give rise mainly to complexes (II). Unfortunately there is no universal series of the strengths of MX_n. One of the sequences taken from reviews[5,19] is presented below:

$$SbF_5 \simeq AsF_5 > BF_3 \simeq GaCl_3 \simeq SbCl_5 \geqslant AlCl_3 > PF_5 \simeq TiCl_4 > BCl_3 .$$

strength of Lewis acid

The quantitative influence of the acidity of the medium on the stability of the acylium salts formed in the RCOOH − H_2SO_4 − SO_3 systems has been investigated by French workers.[93] The results of studies by ^1H and ^{13}C NMR and IR spectroscopy agree fully with one another and with the studies of Deno et al.[85] and Traficante and Masiel,[83,84] indicating the presence in this system of equilibria between the free acid, its protonated form, and the acylium salt:

$$RCOOH \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} R{-}C(OH)_2^{\oplus}\ HSO_4^{\ominus} \underset{-H_2O}{\overset{H_2SO_4-SO_3}{\rightleftharpoons}} RCO^{\oplus}HS_2O_7^{\ominus} ,$$

(A) (B)

(A)

^1H NMR: $\delta_{CH_3} = 2.8$ p.p.m.,
^{13}C NMR: $\delta_{CO} = 194$ p.p.m.,
IR: $\nu(CO) = 1620, 1560\ cm^{-1}$,

(B)

$\delta_{CH_3} = 3.95$ p.p.m.,
$\delta_{CO} = 152$ p.p.m.,
$\nu(CO) = 2309\ cm^{-1}$.

Fig. 4 illustrates the regions corresponding to the existence of free RCOOH and the ions $RC(OH)_2^{\oplus}$ and $RCO^{\oplus}$ as a function of the acidity of the medium. As can be seen from Fig. 4, the cations $CH_3CO^{\oplus}$ are formed only for high acidities of the medium.

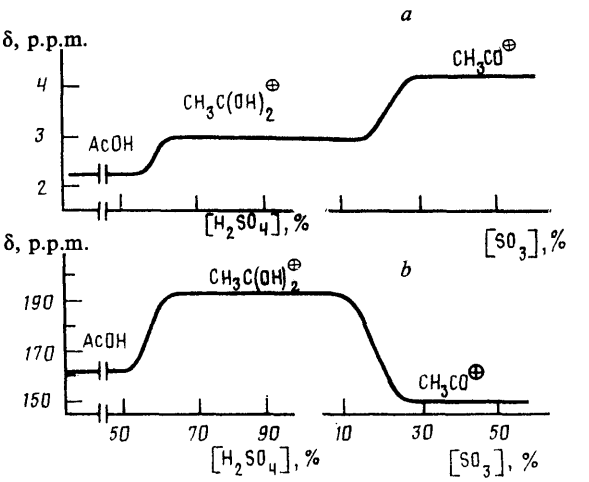


Figure 4. The region corresponding to the existence of the ions $CH_3C(OH)_2^{\oplus}$ and $CH_2CO^{\oplus}$ in the $H_2O-H_2SO_4-SO_3$ system according to ^1H NMR (*a*) [87,93] and ^{13}C NMR (*b*) [85] spectroscopic data.

The nature of the group R exerts a significant influence on the nature of the complexes formed in the RCOX.MX_n system. It follows from the analysis of spectroscopic data[5,17] that an increase in the size of the alkyl group in the sequence $CH_3 \rightarrow C_2H_5 \rightarrow CH(CH_3)_2 \rightarrow C(CH_3)_3$ leads to an increase in the content of donor–acceptor complexes (II) in the equilibrium.

Substituents R exhibiting the $-I$ effect also suppress the formation of acylium salts (I). Thus a special study[94] of systems containing $AlCl_3$ and different RCOCl (R = CH_3, C_2H_5, C_3H_7, $ClCH_2$, Cl_2CH, and Cl_3C) by IR spectroscopy showed that the salts $RCO^{\oplus}AlCl_4^{\ominus}$ are not formed if $pK_a < 2.9-3.2$ for the corresponding RCOOH. For example, only the coordination complex $ClCH_2C(Cl)=O \rightarrow AlCl_3$ exists in the $ClCH_2COCl.AlCl_3$ system.[94]

Acylium salts with $-I$ substituents can be obtained only by the reaction of RCOF with a strong Lewis acid such as SbF_5. Thus the salts $ClCH_2CO^{\oplus}SbF_6^{\ominus}$ and $BrCH_2CO^{\oplus}SbF_6^{\ominus}$ proved to be fairly stable and were isolated in a pure state.[95] The relative stability of the salts $HalCH_2CO^{\oplus}SbF_6^{\ominus}$ can be explained by the positive mesomeric effect of the halogen atoms at the α-carbon atom. According to the authors,[95] the presence of this $+M$ effect stabilises to some extent the cations $HalCH_2CO^{\oplus}$ as a result of the contribution by the resonance structure in which the halogen atom acquires a partial onium character and the positive charge is delocalised:

$$Hal{-}CH_2{-}CO^{\oplus} \longleftrightarrow Hal^{\oplus}{-}CH_2{=}C{=}O .$$

Such stabilisation is insufficient for the salts $Hal_2CHCO^{\oplus}SbF_6^{\ominus}$ and they cannot be obtained. The attempts to synthesise the salt $CF_3CO^{\oplus}SbF_6^{\ominus}$ also proved unsuccessful.[28] These salts could not be detected even spectroscopically. The earlier reports by Lindner and Kranz[96] of the synthesis of $CF_3CO^{\oplus}SbF_6^{\ominus}$ at low temperatures (< −57 °C) should probably be regarded as erroneous.

The influence of the electronic effects of the substituent on the nature of the complexes formed can be traced very clearly, in our view, also in relation to the systems $SbF_5{\cdot}F(O)C-(CH_2)_n-C(O)F{\cdot}SbF_5$ (n = 2−7).[58] For $n \geqslant 3$, the formation of the salts of the dications $SbF_6^{\ominus}{}^{\oplus}CO-(CH_2)_n-CO^{\oplus}SbF_6^{\ominus}$ is observed, while for n = 2 the inductive influence of the oxocarbenium group is already so great that only the monocationic complexes $SbF_6^{\ominus}{}^{\oplus}CO-(CH_2)_2-C(F)=O \rightarrow SbF_5$ are formed.[58]

The replacement of an alkyl group by an aryl group (without substituents in the *ortho*-position) favours the formation of donor–acceptor complexes. However, one should note that the steric effects in the aryl group in ArCOX exert a decisive influence on the structure of the complexes formed. Substituents in the *ortho*-position suppress the formation of donor–acceptor complexes, promoting the formation of acyl cations, which are less sensitive to steric hindrance. Thus the interaction of $TiCl_4$ with 2,6-dimethylbenzoyl chloride or mesitoyl chloride results in the formation of mainly the salts $2,6\text{-}Me_2C_6H_3CO^{\oplus}Ti_2Cl_9^{\ominus}$ and $2,4,6\text{-}Me_3C_6H_2CO^{\oplus}{\cdot}{\cdot}Ti_2Cl_9^{\ominus}$,[23,67] although a weak Lewis acid such as $TiCl_4$ usually forms only type (II) complexes.[7,17]

2. The nature of the solvent

Ionising solvents favour the formation of ionic complexes (I), while weakly polar solvents favour the formation of coordination complexes (II). An effective illustration of the influence of the nature of the solvent on the structure of the complexes formed in the $RCOX.MX_n$ systems may be provided by the behaviour of the $4\text{-}CH_3C_6H_4COCl.SbSl_5$ system.[17,41] Both salts (I) and complexes (II), whose structure was demonstrated by X-ray diffraction, were isolated for this system. Thus, when $4\text{-}CH_3C_6H_4COCl.SbCl_5$ was dissolved in non-polar CCl_4 (ε = 2.2),[50] orthorhombic crystals of the donor–acceptor complex (II) were isolated, while monoclinic crystals of the ionic salt (I) were isolated from the more polar $CHCl_3$ (ε = 5.05).[50] The acylium salt is converted in CCl_4 into a donor–acceptor complex, which in turn isomerises to an acylium salt on dissolution in $CHCl_3$.

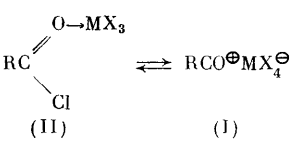
It has been established that the $RCOF.SbF_5$ systems in SO_2 consist exclusively of ionic complexes (I).[7] In liquid HF, the salts $RC(OH)_2^{\oplus}X^{\ominus}$ are also in equilibrium with the acylium salts. In polar organic solvents [nitromethane (ε = 39), nitrobenzene (ε = 35)], the $AcX.SbF_5$ (X = Cl, F) systems represent an equilibrium mixture of complexes (I) and (II). In non-polar organic solvents, the systems with SbF_5 were not investigated.

The $RCOX.AlX_3$ systems have been studied in a wide range of solvents (CH_3Cl_2, $CHCl_3$, $C_2H_4Cl_2$, CH_3NO_2). The set of the available data shows that ionic type (I) species are not formed in the solvents investigated.[9,17,63,78] Admittedly it has been reported[9] that ν(CO) = 2300 cm^{-1} vibrations with an extremely low intensity appear in the IR spectrum of a solution of the $AcCl.AlCl_3$ system in dichloroethane. However, much importance can hardly be attributed to this fact, particularly since, together with the main frequencies as regards intensity, referring to complex (II), the ν(CO) = 1800 cm^{-1} frequency of the initial acetyl chloride is present in the IR spectrum of the solution, which is usually due to secondary reactions of the $RCOX.MX_n$ systems under the influence of the salt optical components.

3. The influence of temperature

The literature data concerning the influence of temperature on the equilibria between the complexes, (I) ⇄ (II), are scanty and contradictory.

Perkampus and Weiss[97] concluded that, as the temperature is reduced, the equilibrium (II) ⇄ (I) shifts towards the formation of the type (II) complex:



(a) R = Ph, $MX_3 = AlBr_3$; (b) R = Me, $MX_3 = AlBr_3$ (−30 °C); (c) R = Et, $MX_3 = AlBr_3$ (−40 °C); (d) R = Et, $MX_3 = GaCl_3$ (−100 °C).

Thus it has been shown that the content of the salt $PhCO^{\oplus}AlBr_3Cl^{\ominus}$ is a maximum at 40–50 °C, diminishing with decrease in temperature. For other systems, such data were not quoted[97] and only the temperatures at which absorption in the region of ν(CO) for the acylium salt begins to be observed were indicated (in brackets).

On the other hand, it has been shown by ^{81}Br NQR that even at 77 K the ionic structure of the salts $CH_3CO^{\oplus}AlBr_4^{\ominus}$ is retained and that a type (II) complex is not formed.[55]

VII. The influence of the structure of acylium salts on their thermodynamic stability

The strength of the Lewis acid MX_n and the nature of the group attached to the carbonyl group exert a significant influence not only on the equilibrium between complexes (I) and (II) but also on the chemical stability of the complexes formed.

It follows from Table 1 that the maximum stability and the highest melting points are characteristic of adducts formed by the strongest Lewis acids. On the other hand, weak Lewis acids form readily fusible and relatively unstable compounds. Thus the complex $AcF.BF_3$, which has the structure of an ionic salt in the solid state, dissociates reversibly into AcF and BF_3 at 20 °C (the boiling point of AcF).

The stability of the complexes $RCOX.MX_n$ also depends on the structure of the group R. The cations $RCO^{\oplus}$, where there is no possibility of an effective stabilisation of $R^{\oplus}$, are resistant to decarbonylation. Thus thermodynamic calculation shows that the decomposition of the acyl cation is a strongly endothermic reaction and does not occur under the usual conditions:[34]

$$CH_3CO^{\oplus} \rightarrow CH_3^{\oplus} + CO, \quad \Delta H = 294-340 \text{ kJ mol}^{-1}.$$

On the other hand, acylium salts with a group R capable of forming a relatively stable carbonium ion are extremely unstable. Thus $(CH_3)_3CCO^{\oplus}SbF_6^{\ominus}$ decomposes to a slight extent at −40 °C, while at room temperature the complex undergoes full irreversible decomposition with liberation of CO. The formation of the t-butyl cation on its decomposition has been demonstrated by NMR:[27]

$$(CH_3)_3C{-}CO^{\oplus}SbF_6^{\ominus} \rightarrow (CH_3)_3C^{\oplus}SbF_6^{\ominus} + CO.$$

The very high stability of the triphenylcarbenium cation is just as

responsible for the very low stability of the $Ph_3CCO^{\oplus}$ ion, which eliminates CO even at a low temperature:[98]

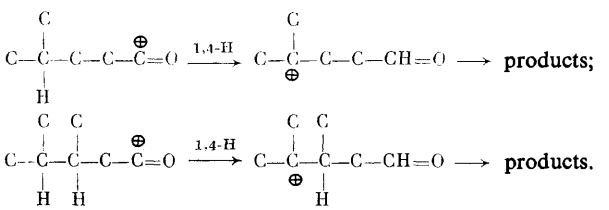
$$Ph_3C{-}CO^{\oplus} \rightarrow Ph_3C^{\oplus} + CO.$$

Similarly the complex $(CH_3)_3CCOCl.AlCl_3$ is spontaneously decarbonylated at room temperature. It is of interest that in the presence of isopentane the process is suppressed and the main pathway in the reaction of the complex becomes the formation of the ketone $(CH_3)_2CHCOCH_3$. It is believed[99,100] that the ketone detected is formed via the intramolecular 1,2-shift of the methyl group in the acyl cation, while the isoalkane is a donor of the hydride ion:

$$(CH_3)_2\overset{\oplus}{C}{-}\overset{\oplus}{C}{=}O \xrightarrow{\sim 1,2\text{-Me}} (CH_3)_2\overset{\oplus}{C}{-}C(=O){-}CH_3 \xrightarrow{+H^{\ominus}} (CH_3)_2CH{-}C(=O){-}CH_3.$$

Similar intramolecular rearrangements apparently occur in the familiar alkane carbonylation reactions catalysed by Lewis acids.[101]

Together with the intermolecular hydride transfer from RH to $RCO^{\oplus}$, an intramolecular 1,4-hydride shift from the tertiary carbon atom to the carbonyl carbon atom of the $RCO^{\oplus}$ cation can take place at temperatures in the range 60–100 °C:[102]



On the other hand, if the tertiary carbon atoms are not located in the 4-position, then an intermolecular hydride shift takes place in which another $RCO^{\oplus}$ species functions in all probability as the $H^{\ominus}$ acceptor.[102] In the case of n-alkyl groups, both intramolecular and intermolecular hydride shifts are suppressed and such cations n-$RCO^{\oplus}$ do not change under the conditions indicated.

The presence of atoms with a $+M$ effect at the α-carbon atom in the cations $RCO^{\oplus}$ destabilises the cation and, with increase in the number of such groups, the instability also increases. The salts $CF_3CO^{\oplus}SbF_6^{\ominus}$ and $F_2CHCO^{\oplus}SbF_6^{\ominus}$ cannot be detected even at −70 °C, while at −60 °C CF_4 and CF_3H—the products of the decarbonylation of these salts—were identified respectively.[28]

VIII. Conclusion

The complexes of acyl halides with Lewis acids, $RCOX.MX_n$, have a hundred year's long history. The wide scale employment of metal complexes in synthetic organic chemistry began with these particular systems.

During the 50 years which have elapsed since the synthesis of the first well characterised complex $Ac^{\oplus}BF_4^{\ominus}$, extensive factual data have accumulated in this field: a large series of ionic complexes $RCO^{\oplus}MX_{n+1}^{\ominus}$ and donor–acceptor complexes $RC(X)=O \rightarrow MX_n$ have been synthesised, the characteristic features of the structures of complexes of both types in the solid state and in solution have been investigated, spectroscopic methods for the identification of these complexes have been developed, and factors influencing the equilibrium between them have been discovered. However, many problems in this field still remain unsolved and many contradictions in the literature concerning the complexes $RCOX.MX_n$ have not been explained. The equilibria between ionic and donor–acceptor complexes have not been studied systematically, the investigations having been carried out mainly at a qualitative level. There are almost no literature data on the coordination complexes $RC(O)Cl \rightarrow MX_n$ and their role in the equilibrium

$$RCO^{\oplus}MX_{n+1}^{\ominus} \rightleftarrows RC(X)=O \rightarrow MX_n.$$

Overall, one may conclude that the $RCOX.MX_n$ systems have been studied fairly well at a qualitative level. The next stage in their investigation will probably lead to the determination of quantitative data on the equilibria existing in these systems, including equilibria with participation of relatively unstable complexes formed as intermediates.

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