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Acid strength of proton donors in complexes of nontransition metal halides as a measure of the activity of electrophilic polymerisation catalysts

K S Minsker, V A Babkin, G E Zaikov

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Abstract. Data on one of the most urgent problems in modern theoretical chemistry are reviewed: the calculation of the acid strength of the complexes formed by the interaction of Lewis acids with proton donors, and the correlation of the acid strength with the activity and selectivity of these complexes as catalysts of electrophilic processes. Complexes based on aluminium and magnesium chlorides and on boron fluorides are discussed. It is shown that increasing the acid strength of these complexes as catalysts of electrophilic polymerisation reactions increases their activity but lowers their selectivity. The bibliography includes 43 references.

I. Introduction

Complex catalysts based on non-transition metal halides (R_nAlCl_{3-n}, R_nMgCl_{2-n}, R_nBF_{3-n}, where $n = 0 - 3$, R = OH, CH_3, C_2H_5, *iso*-C_3H_7, *tert*-C_4H_9) and on proton donors (H_2O, HCl, HF, ROH) are the classical initiators of electrophilic processes. The donor–acceptor interaction of the components leads to the formation of complexes having an acid strength greater than that of the initial compounds.[1,2] The strengthening of the acidic properties of the systems during complex formation is accompanied by a marked increase in their catalytic activity.[3] The formation of complexes between individually inactive protogenic compounds such as alcohols (or water) and the appropriate Lewis acids offers an enhanced selectivity in the cationic polymerisation of olefins.[3,4] However, in spite of significant progress in the study of the behaviour of complexes of this type in various electrophilic reactions, the role of the acid strength is still unclear.[1,5] Therefore the current interest in the theoretical calculation of the acid strength of complex catalysts of different chemical nature is not surprising. A reasonably precise estimate can be obtained by calculating the charges on the hydrogen atoms in the proton donors (q_{H^+}). These values are well correlated with the universal acidity indicator of chemical compounds δpK_a.

K S Minsker, V A Babkin Department of High-molecular-mass Compounds, Bashkir State University, 450076 Ufa, ul. Frunze 32. Tel. (7-347-2) 26 24 05
G E Zaikov Semenov Institute of Chemical Physics of the Russian Academy of Sciences, 117977 Moscow, ul. Kosygina 4, Fax (7-095) 938 21 56

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The characteristics of the acid strength (q_{H^+}, Δq_{H^+}) of the adducts of R_nAlCl_{3-n}, R_nMgCl_{2-n}, and R_nBF_{3-n} with proton donors are determined by calculating the models of the complexes with a 1 : 1 stoichiometric composition by the semiempirical CNDO/2 quantum-mechanical method specially parametrised to give the best description of the charge characteristics.[7] This approach has been used successfully in calculations of the acidic catalyst properties of complex electrophilic catalysts.[6]

The structures of the model complexes (usually in the form of tetrahedra, or distorted tetrahedra) are close to the structures recently discussed by various workers.[8–11] The calculations were carried out without allowing for the effect of the solvent, i.e. in the isolated molecule approximation. This approach does not detract from the value of the chosen method of modelling the complex catalyst, since these catalysts are extremely active in hydrocarbon (indifferent) media.

The aim of the present review is to generalise data on the acid strength of the complexes R_nAlCl_{3-n}, R_nMgCl_{2-n}, and R_nBF_{3-n} with proton donors (HCl, H_2O, HF, ROH), and on the relationship between the acid strength of these compounds and their activity and selectivity as catalysts of electrophilic processes (in particular, of the cationic polymerisation of olefins). Establishing correlations between these parameters is important from the standpoint of rationalising the choice of the most effective catalysts for chemical processes, and also as an approach to establishing fundamental concepts on the effect of the acid strength on the behaviour of complex catalysts in electrophilic reactions.

II. Complexes based on aluminium chlorides

The formation of complexes based on aluminium chlorides R_nAlCl_{3-n} and on proton donors (HCl, H_2O, ROH) has been demonstrated both experimentally and theoretically.[12–15]

1. Complexes based on aluminium chlorides and hydrogen chloride

The formation of complexes between R_nAlCl_{3-n} and HCl has to compete with processes involving the substrate and the relatively stable counterion in the reaction with a proton.[15,16] Depending on the nature of the Lewis acid and on some other factors, the complexes formed with HCl have H–Cl bonds with different levels of looseness. In proton complexes, or in the Gustavson complexes (GC), ionisation of the $H^{\delta+}...Cl^{\delta-}$ bond is responsible for the high acid strength.[2,17] This gives the GC an enhanced activity towards the electrophilic polymerisation of olefins and of some other monomers, which is seen, in particular, as the

formation of polymeric products with a higher molecular mass (isobutene, styrene, vinyl butyl ether), as the ability to initiate the oligomerisation of propene, etc. These effects are associated both with a greater stability of the complex counterion towards dissociation into its components under the influence of the carbenium ion and with the acid strength of the GC. The characteristic features of the cationic fragment (positive charge delocalised over the aromatic system) explain the unique properties of these complexes as electrophilic agents. For example, the proton-donor activity of the GC decreases in the sequence

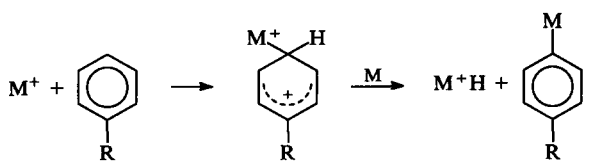
$$3\,C_6H_5CH_3 \cdot HCl \cdot Al_2Cl_6 > 4\,(CH_3)_3C_6H_3 \cdot HCl \cdot Al_2Cl_6 > > 3\,(CH_3)_6C_6 \cdot HCl \cdot AlCl_3 .$$

This series is the opposite of the basicity series of aromatic hydrocarbons

$$(CH_3)_6C_6 > (CH_3)_3C_6H_3 > CH_3C_6H_5 .$$

The role of the basicity of the aromatic component of the GC in the initiation of the polymerisation is ambiguous: increasing the basicity increases the stability of the arenonium ion, but it weakens the bond between the carbenium ion and the counterion. [18]

Polymeric GC are formed in a similar way from their low-molecular analogues. However, the presence in the GC of a solvation shell of aromatic nuclei bound to the polymer chain (polystyrene, styrene–divinylbenzene copolymer) affects the stoichiometric composition and other properties of the resulting complexes. [19] Irrespective of the composition of the GC, initiating the polymerisation of olefins reduces to accepting a proton from the arenonium ions. The free aromatic hydrocarbon formed from the arenonium ions by H-initiation can be alkylated by a growing carbenium ion. The reaction which terminates the polymeric chain leads to the formation of new (polymeric) σ complexes, more stable than the initial GC and able (under appropriate conditions) to reinitiate the polymerisation of the olefin:



The mechanism of the catalytic action of the $R_nAlCl_{3-n} \cdot HCl$ complexes (where R = CH_3, C_2H_5, etc.) is simple and self-evident. [10] Therefore a confirmation of the experimentally observed behaviour of the HCl complexes by calculation can be used as a test of the validity of the CNDO/2 method in calculations for other complexes. A calculation of the parameters of the known complexes of hydrogen chloride with aluminium chloride was therefore carried out first.

Some quantum chemical characteristics of the complexes $R_nAlCl_{3-n} \cdot HCl$ [the charges on the hydrogen atom in the HCl (q_{H^+}), the increase in the charge on the hydrogen atom in HCl upon forming the complexes with R_nAlCl_{3-n} (Δq_{H^+}) and the acidity indicator (δpK_a) are shown in Table 1].

Table 1. Acid strength of the $R_nAlCl_{3-n} \cdot HCl$ complexes. [10]

Complex	q_{H^+}	Δq_{H^+}	δpK_a
HCl	+0.09	–	−7
$HCl \cdot (CH_3)_3Al$	+0.18	0.09	−16.3
$HCl \cdot (CH_3)_2AlCl$	+0.18	0.09	−16.3
$HCl \cdot CH_3AlCl_2$	+0.18	0.09	−16.0
$HCl \cdot C_2H_5AlCl_2$	+0.18	0.10	−16.0
$HCl \cdot AlCl_3$	+0.19	0.10	−16.0
$HCl \cdot HOAlCl_2$	+0.20	0.11	−18.0

When the complexes of R_nAlCl_{3-n} with HCl are formed the charge on the hydrogen atom increases from +0.09 in the free HCl to +0.18 to +0.20 in the complexes. The removal of H^+ is accompanied by an evolution of energy of 260–340 kJ mol^{-1}, i.e. it is energetically favourable. [10] The acidity indicators of the complexes are only very slightly dependent on the nature of the Lewis acid (R_nAlCl_{3-n}, $HOAlCl_2$) varying from −16 to −18.

Thus the quantum chemical calculations of the $R_nAlCl_{3-n} \cdot HCl$ complexes are consistent with the experimental data on their high acidity and thus confirm the validity of the CNDO/2 method for calculations of other models based on the aluminium chlorides. The lack of dependence of the acid strength of the complexes on the nature of the Lewis acid shows that all the complexes of R_nAlCl_{3-n} with HCl have a propensity towards self-ionisation. This conclusion is consistent with experimental data on the high activity of the complexes of HCl with Lewis acids (from $AlCl_3$ to AlR_2Cl) in the cationic polymerisation of olefins. [1] At the same time the data obtained in these calculations show that the preferred scheme for the direct initiation of the electrophilic polymerisation reaction is

$$HCl + R_nAlCl_{3-n} \rightleftharpoons H^{\delta+}, [R_nAlCl_{4-n}]^{\delta-} \xrightarrow[-M]{} \longrightarrow M_1^{\delta+}, [R_nAlCl_{4-n}]^{\delta-}$$

However, it should be noted that the increase in the acidity of the $R_nAlCl_{3-n} \cdot HCl$ catalysts in the electrophilic polymerisation of the olefins is accompanied by a large decrease in the selectivity of their action (Table 2).

Table 2. Polymerisation of isobutene from the C_4 hydrocarbon fraction under the influence of $R_nAlCl_{3-n} \cdot HCl$.

Catalyst	Selectivity for *iso*-C_4H_8/ vol.%
$HCl \cdot 3\,C_6H_5CH_3 \cdot 2\,AlCl_3$	36 ± 2
$HCl \cdot C_6H_5CH_3 \cdot C_2H_5AlCl_2$	43 ± 2
$HCl \cdot C_6H_5CH_3 \cdot (C_2H_5)_2AlCl$	53 ± 3

Notes. Composition of fraction, wt.%: C_3H_6, 0.6; C_4H_{10}, 55.1; *iso*-C_4H_8, 14.9; α,β-C_4H_8, 29.5; $[R_nAlCl_{3-n}] = 7.3 \times 10^{-3}$ mol dm^{-3}, $[C_4] = 1.3$ mol dm^{-3}, solvent CH_2Cl_2, 253 K, reaction time 10 min.

2. Complexes based on aluminium chlorides and water

The formation of 1:1 complexes (aqua complexes) by the interaction of R_nAlCl_{3-n} with water has been established. [4,12] Like other electron donors, water easily undergoes donor–acceptor interaction with aluminium compounds.

In inert solvents the aqua complexes of aluminium ($R_nAlCl_{3-n} \cdot H_2O$) have a reasonably high thermal stability and stability towards hydrolysis of the Al–Cl bond, and a low electric conductivity ($\sigma \approx 10^{-10}$ S cm^{-1}). As shown by a qualitative reaction with xanthone they are not H-acids. [12]

The H-activity of the complexes, established for model systems of the type of $CH_3CH(CH_3)=CH_2-C_2H_5AlCl_2 \cdot D_2O$ and resulting from the low Brønsted acidity, is not obvious, [16,20] and therefore it does not look as if the ionisation of the aqua complex in the absence of a monomer can take place by the scheme

$$C_2H_5AlCl_2 + H_2O \longrightarrow H^+, [C_2H_5AlCl_2 \cdot OH]^-$$

When the cationic polymerisation of olefins is initiated by aqua complexes of the aluminium chlorides the latter undergo various transformations, in particular into aqua complexes of alumoxane or ternary complexes of the $HCl \cdot R_nAlCl_{3-n} \cdot H_2O$

Table 3. Acid strength of the aqua complexes of some aluminium chlorides. [10,20,23]

Aqua complex	q_{H^+} (±0.02)	δpK_a
Group I		
$H_2O \cdot AlCl_3$	+0.20	+7.1
$H_2O \cdot HOAlCl_2$	+0.18	+8.5
$H_2O \cdot (HO)_2AlCl$	+0.17	+12
$H_2O \cdot (HO)_3Al$	+0.17	+12
Group II		
$H_2O \cdot CH_3AlCl_2$	+0.19	+7.7
$H_2O \cdot (CH_3)_2AlCl$	+0.16	+14.4
$H_2O \cdot (CH_3)_3Al$	+0.16	+14.4
Group III		
$H_2O \cdot C_2H_5AlCl_2$	+0.20	+7.5
$H_2O \cdot (C_2H_5)_2AlCl$	+0.18	+8.5
$H_2O \cdot (C_2H_5)_3Al$	+0.17	+12
Group IV		
$H_2O \cdot (C_3H_7)_nAlCl_{3-n}$	+0.19±0.17	+7.7 to +12
Group V		
$H_2O \cdot (C_4H_9)_nAlCl_{3-n}$	+0.19±0.17	+7.7 to +12
Group VI		
$H_2O \cdot Al_2Cl_4O$	+0.21	+4.4
$H_2O \cdot CH_3Al_2Cl_3O$	+0.20	+7.1
$H_2O \cdot (CH_3)_2Al_2Cl_2O$	+0.20	+7.1
$H_2O \cdot (CH_3)_3Al_2ClO$	+0.18	+8.5
$H_2O \cdot (CH_3)_4Al_2O$	+0.18	+8.5
GroupVII		
$HCl \cdot H_2O \cdot AlCl_3$	–	+1.5
$HCl \cdot H_2O \cdot CH_3AlCl_2$	–	+1.3

type.[20] Therefore other models, appropriate to these transformations, were calculated together with the models of the initial complexes (Table 3). The tendency to form aqua complexes between R_nAlCl_{3-n} and H_2O increases as the strength of the Lewis acid is increased: $(HO)_3Al < (CH_3)_3Al < (C_2H_5)_3Al < (C_3H_7)_3Al < (C_4H_9)_3Al < AlCl_3$. This is suggested by the nature of the changes in q_{H^+} and in δpK_a and by other experimental results.[22] For example, acidic catalysts are universally found in the composition of various complexes of $AlCl_3$ or $RAlCl_2$, and the $R_3Al(R_2AlCl) \cdot H_2O$ system (whose acidic properties are weaker) catalyses preferentially the low-temperature polymerisation of strongly basic monomers (styrene, isobutene).[23]

The aqua complexes $R_nAlCl_{3-n} \cdot H_2O$ have a relatively low acid strength (see Table 3). The extraction of a proton from complexes of this type is not energetically favourable, requiring an expenditure of energy of between 70 and 790 kJ mol^{-1} (see Sangalov et al.[10]). Nevertheless these complexes have a relatively high activity in electrophilic polymerisation processes (isobutene), with a selectivity of almost 100% (Table 4), suggesting either the formation (during initiation) of active centres with an enhanced acid strength, susceptible to protonation, or a more complex initiation mechanism for the process.[20]

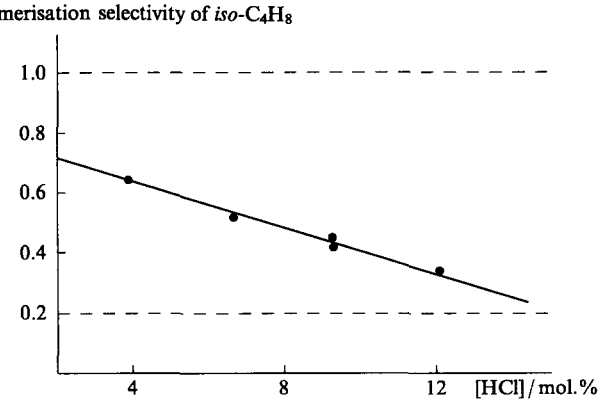


Figure 1. Dependence of the selectivity of the polymerisation of isobutene on the concentration of HCl added to $H_2O \cdot C_2H_5AlCl_2$. The upper broken line shows the selectivity of the process in the presence of $H_2O \cdot C_2H_5AlCl_2$ (without additives); the lower broken line is the selectivity in the presence of $HCl \cdot C_2H_5AlCl_2$. Polymerisation conditions: $[C_4] = 3 \times 10^{-6}$ mol g^{-1}, $[C_2H_5AlCl_2] = 8 \times 10^{-6}$ mol dm^{-3}, 250 K.

The ternary aluminium complexes listed in group VII of Table 3 have a high acid strength. However, in a comparative study of the selectivity of catalysts for the polymerisation of isobutene ($H_2O \cdot C_2H_5AlCl_2$, $HCl \cdot C_2H_5AlCl_2$, and $HCl \cdot H_2O \cdot C_2H_5AlCl_2$) it was shown experimentally that the activity of the starting aqua complex $R_nAlCl_{3-n} \cdot H_2O$ is independent of the intermediate formation of HCl (Fig. 1). The addition of HCl to $C_2H_5AlCl_2 \cdot H_2O$ markedly lowers the selectivity, which approaches that of the process initiated by $HCl \cdot C_2H_5AlCl_2$.

The lowest Brønsted acidity among the catalysts of the first six groups (see Table 3) is found in the aqua complexes $Al_2Cl_4O \cdot H_2O$ ($\delta pK_a = +4.4$), $Al_2Cl_3O \cdot H_2O$ ($\delta pK_a = +7.1$), and $C_2H_5AlCl_2 \cdot H_2O$ ($\delta pK_a = +7.5$). These same aqua complexes are universal acidic catalysts for a large number of electrophilic reactions, including the polymerisation of olefins. The aluminium complexes $Al_2Cl_4O \cdot H_2O$ and $C_2H_5AlCl_2 \cdot H_2O$ have similar acidic catalyst properties. Theoretical calculations are consistent with experimental data on the equality of the first alkylation rate constants of benzene by propene in the presence of $C_2H_5AlCl_2 \cdot H_2O$ [$k = (21.5 \pm 0.6) \times 10^{-4}$ s^{-1}] and

Table 4. Oligomerisation of isobutene from mixtures of hydrocarbons in the presence of the complexes of aluminium chlorides with proton donors.

Catalyst	Composition of the hydrocarbon mixture before the reaction/vol.%				Conversion of *iso*-C_4H_8/ mass%	Selectivity for *iso*-C_4H_8/ mass%
	C_3H_8	C_4H_{10}	*iso*-C_4H_8	α,β-C_4H_8		
$H_2O \cdot C_2H_5AlCl_2$	3.0	55.5	37.9	3.5	96	100
$H_2O \cdot C_2H_5AlCl_2$	3.9	67.5	11.3	17.3	98	100
$H_2O \cdot C_2H_5AlCl_2$	0.9	45.1	31.1	23.0	99	100
$H_2O \cdot C_2H_5AlCl_2$ [a]	4.9	63.2	8.5	23.5	100	57
$C_2H_5AlCl_2$	3.0	55.5	37.9	3.5	95	60
$(C_6H_5)_3COH \cdot C_2H_5AlCl_2$	0.6	55.1	14.9	29.5	90	79
$CH_3OH \cdot C_2H_5AlCl_2$	0.6	55.1	14.9	29.5	95	74

Notes. Polymerisation conditions: volume of the mixture of C_4 hydrocarbons 30 cm^3; concentration of catalyst 5.6×10^{-2} mol dm^{-3}; solvent, heptane (20 cm^3); 293 K; reaction time 10 min.
[a]Solvent CH_2Cl_2.

of $Al_2Cl_4O \cdot H_2O$[$k = (19.8 \pm 1.2) \times 10^{-4}$ s^{-1}] at 297 K. However, the low acid strength of the aqua complexes based on aluminium chlorides and on some of their transformation products (alumoxanes, aluminium alkoxides) implies that the electron donors (olefins, arenes) play an active role in the development of acidic catalyst properties in these materials.

3. Complexes based on aluminium chlorides and alcohols

The ability of alcohols to display both proton-donor (H^+) and carbo-cation activity (R^+) is the most distinguishing feature of the behaviour of the $R_nAlCl_{3-n} \cdot ROH$ aluminium complexes as electrophilic catalysts for the polymerisation of olefins. In particular, in the $AlCl_3 \cdot ROH$ complexes we observe the classical H-initiation scheme for the cationic polymerisation of olefins: [21]

$$ROH + AlCl_3 \rightleftharpoons ROH \cdot AlCl_3 \rightleftharpoons H^+, [AlCl_3 \cdot OR]^-$$

In this process the catalytic acitivity of $AlCl_3 \cdot ROH$ increases with the acidity of the alcohol. [23, 24]

The carbo-cation activity of $C_2H_5AlCl_2 \cdot ROH$ has also been demonstrated and shown to vary in the following sequence with the coordination of ROH to $RAlCl_3$: *tert*-C_4H_9OH < < C_6H_5OH < $(C_6H_5)_3COH$. This order is confirmed by quantum chemical calculations on the aluminium complexes $R_nAlCl_{3-n} \cdot ROH$ or similar compounds. [10, 15, 25]

The parameters of the acid strength, the bond orders, and the predominant type of activity in complexes of alcohols with various reagents are shown in Table 5. About 70 model compounds were studied, including the individual alcohols ROH (CH_3OH, C_2H_5OH, C_3H_7OH, *tert*-C_4H_9OH), and also the compounds $H^+ \cdot ROH$, $R_nAlCl_{3-n} \cdot ROH$, $H_3C^+ \cdot ROH$, and $(CH_3)_3C^+ \cdot ROH$, i.e. complexes with Brønsted and with Lewis acids.

As can be seen, the bond orders P_{OH} and the charges on a hydrogen atom q_{H^+} are almost the same for all the alcohols. This is consistent with the experimental values [26] δpK_a = (+16) to (+19). The bond order P_{OC} tends to decrease with increasing branching of the radical R in the alcohol molecule; a minimum value of P_{OC} is found for *tert*-C_4H_9OH.

In protonated alcohols (models 5–8 in Table 5) the bond order P_{OC} and the charge on a hydrogen atom (of the same order of magnitude as the charge on a hydrogen atom in a hydroxonium ion) [5] remain almost unchanged. At the same time P_{OC} decreases as the extent of replacement of the carbon atom attached to the OH group in the alcohol molecule increases. The charge per hydrogen atom q_{H^+} is thereby increased by a factor of 2–3, which corresponds to a substantial increase in the acid strength of the complex to $\delta pK_a = -29$ to -20. When the alcohols are coordinated to acids stronger than H^+ [the carbo-cations H_3C^+ and $(CH_3)_3C^+$] this behaviour persists, but the

Table 5. Quantum-chemical parameters of the complexes of alcohols with some reagents. [10, 25]

No. of model	Model	Group	q_{H^+}	δpK_a	P_{OH}	P_{OC}	Activity type
1–4	ROH	I	+0.14, +0.13, +0.13, +0.12	+16, +18, +18, +19	0.96, 0.96, 0.96, 0.96	1.0, 0.99, 0.97, 0.94	H^+, H^+, H^+-R^+, R^+
5–8	$H^+ \cdot ROH$	II	+0.36, +0.34, +0.33, +0.32	−29, −24, −22, −20	0.85, 0.85, 0.87, 0.87	0.87, 0.81, 0.74, 0.71	H^+-R^+, R^+, R^+, R^+
9–12	$H_3C^+ \cdot ROH$	III	+0.34, +0.32, +0.32, +0.32	−24, −20, −20, −20	0.86, 0.88 0.87, 0.87	0.87, 0.78, 0.73, 0.70	H^+-R^+, R^+, R^+, R^+
13–16	*tert*-$C_4H_9 \cdot ROH$	IV	+0.30, +0.27, +0.28, +0.27	−17, −11, −13, −11	0.87, 0.87, 0.88, 0.88	0.89, 0.81, 0.78, 0.70	H^+-R^+, R^+, R^+, R^+
17–20	$Cl_3Al \cdot ROH$	V	+0.20, +0.19, +0.18, +0.17	+7.5, +7.7, +8.5, +12	0.93, 0.94, 0.94, 0.94	0.99, 0.93, 0.90, 0.88	H^+, H^+-R^+, R^+, R^+
21–24	$CH_3AlCl_2 \cdot ROH$	VI	+0.20, +0.18, +0.19, +0.17	+7.5, +8.5, +7.7, +12	0.93, 0.93, 0.94, 0.94	0.99, 0.94, 0.91, 0.90	H^+, H^+-R^+, R^+, R^+
25–28	$(CH_3)_2AlCl \cdot ROH$	VII	+0.18, +0.17, +0.16, +0.15	+8.5, +12, +14.4, +15.1	0.92, 0.92, 0.92, 0.93	0.98, 0.93, 0.90, 0.89	H^+, H^+-R^+, R^+, R^+
29–32	$(CH_3)_3Al \cdot ROH$	VIII	+0.17, +0.16, +0.16, +0.15	+12, +14.4, +14.4, +15.1	0.95, 0.94, 0.93, 0.93	0.97, 0.93, 0.91, 0.90	$H^+-R^+, H^+-R^+, R^+, R^+$
33–36	$C_2H_5AlCl_2 \cdot ROH$	IX	+0.20, +0.19, +0.18, +0.18	+7.5, +7.7, +8.5, +8.5	0.94, 0.94, 0.95, 0.94	0.99, 0.94, 0.90, 0.90	H^+, H^+-R^+, R^+, R^+
37–40	$(C_2H_5)_2AlCl \cdot ROH$	X	+0.17, +0.17, +0.17, +0.15	+12, +12, +12, +15.1	0.93, 0.95, 0.94, 0.92	0.98, 0.94, 0.91, 0.89	H^+, H^+-R^+, R^+, R^+
41–44	$(C_2H_5)_3Al \cdot ROH$	XI	+0.17, +0.16, +0.16, +0.15	+12, +14.4, +14.4, +15.1	0.93, 0.92, 0.93, 0.92	0.97, 0.93, 0.90, 0.99	H^+, H^+-R^+, R^+, R^+
45–48	$C_3H_7AlCl_2 \cdot ROH$	XII	+0.20, +0.19, +0.19, +0.18	+7.5, +7.7, +7.7, +8.5	0.94, 0.94, 0.93, 0.94	0.99, 0.93, 0.90, 0.89	H^+, H^+-R^+, R^+, R^+
49–52	$(C_3H_7)_2AlCl \cdot ROH$	XIII	+0.17, +0.16, +0.16, +0.15	+12, +14.4, +14.4, +15.1	0.93, 0.92, 0.94, 0.94	0.99, 0.93, 0.91, 0.90	H^+, H^+-R^+, R^+, R^+
53–56	$(C_3H_7)_3Al \cdot ROH$	XIV	+0.17, +0.17, +0.16, +0.15	+12, +12, +14.4, +15.1	0.93, 0.93, 0.94, 0.93	0.98, 0.94, 0.94, 0.90	H^+, H^+-R^+, H^+-R^+
57–60	$C_4H_9AlCl_2 \cdot ROH$	XV	+0.20, +0.20, +0.18, +0.17	+7.5, +7.5, +8.5, +12	0.94, 0.94, 0.94, 0.93	0.98, 0.94, 0.90, 0.88	H^+, H^+-R^+, R^+, R^+
61–64	$(C_4H_9)_2AlCl \cdot ROH$	XVI	+0.17, +0.16, +0.15, +0.15	+12, +14.4, +14.4, +15.1	0.93, 0.93, 0.92, 0.93	0.99, 0.93, 0.90, 0.89	H^+, H^+-R^+, H^+-R^+
65–68	$(C_4H_9)_3Al \cdot ROH$	XVII	+0.17, +0.16, +0.15, +0.15	+12, +14.4, +15.1, +15.1	0.93, 0.93, 0.92, 0.93	0.99, 0.94, 0.90, 0.92	H^+, H^+-R^+, H^+-R^+

Notes. The sequence of numbers and symbols in the columns corresponds to the alcohol series with R = CH_3, C_2H_5, *iso*-C_3H_7, *tert*-C_4H_9; the following symbols are used: H^+ denotes a dominant proton-donor activity; R^+ denotes a dominant carbo-cation activity; H^+-R^+ states that the two activities have equal probabilities.

acidity of the resulting complexes is lower (δpK_a = −24 to −11). On the whole the complexes $H^+ \cdot ROH$, $H_3C^+ \cdot ROH$, and $(H_3C)_3C^+ \cdot ROH$ (models 5–16) have a high acid strength and usually display a carbo-cation activity.

In the $R_nAlCl_{3-n} \cdot ROH$ complexes (models 17–68) we find a levelling of the differences in the bond orders P_{OH} and P_{OC} for each alcohol and of the bond orders P_{OC} for different alcohols. Therefore there is no overall dominant path for the fragmentation of the alcohols in these complexes, and depending on the nature of R in the alcohol molecule they can display either proton-donor or carbo-cation activity. Like the $R_nAlCl_{3-n} \cdot H_2O$ complexes the $R_nAlCl_{3-n} \cdot ROH$ complexes are characterised by a low acid strength, with δpK_a in the range of −15.1 to −7.1. In the light of the negative values[27] of the energy of proton removal (−590 to −390 kJ mol^{-1}) the removal is energetically unfavourable in the complexes of alcohols with aluminium chlorides. Therefore their activity can manifest itself only in the presence of direct participation of electron donors (olefins, arenes, etc.).[28] As regards selectivity the complexes of this type occupy an intermediate place between $R_nAlCl_{3-n} \cdot H_2O$ and $R_nAlCl_{3-n} \cdot HCl$ (see Tables 2 and 4).

Thus increasing the strength of the Lewis acid coordinated to the alcohol increases the probability of forming a carbo-cation. This trend is quite easily observed, for example in the case of *tert*-C_4H_9OH, i. e. of an alcohol with a strongly branched hydrocarbon radical. Obviously, we can expect to find the same trend in other alcohols containing branched R radicals. A calculation of the complexes of alcohols with different Lewis acids based on aluminium chlorides (not allowing for the effect of the anion, the solvent, and other factors) confirms the dependence of the fragmentation path followed by the alcohol (H^+ or R^+ activity) on the nature of its radical and on the type of the acid.

Published experimental data on the cationic properties of systems consisting of an alcohol and an acidic agent can also be classified according to the behaviour of the alcohol during the formation of the active centres, i. e. according to whether proton or carbo-cation activity (or both simultaneously) predominates. By comparing calculated with experimental data we can test the validity of the fragmentation paths suggested for the alcohols in the complexes.

The stability of the resulting ionic fragments is one of the fundamental factors determining the fragmentation path chosen by the alcohols. The presence of substituents on the α carbon atom and the possibility of binding an hydroxyl group as a stable anion produce reliably identified carbonium ions: for example, in the $(C_6H_5)_3COH-H_2SO_4$ system.[29] The presence of stable carbo-cations, owing to the high stability (low nucleophilicity) of the counterions, has been observed[1] also by NMR during the formation of complexes of the alcohols with 'superacids':

$$(CH_3)_3COH \xrightarrow{SbF_5,\ FSO_3H} (CH_3)_3C^+, SbF_5 \cdot FSO_3^- + H_2O$$

The formation of $(CH_3)_3C^+ \cdot BF_4^-$ was observed also[1] in the interaction of *tert*-butanol with another strongly acid system: $BF_3 \cdot HF$. Thus, *tert*-substituted alcohols in the presence of strong acids are easily dissociated at the C–O bond.

If the experimental conditions do not adequately stabilise the carbonium ions, the fragmentation path adopted by the alcohol bound in a complex with a Lewis acid is determined by other factors, and in particular by the chemical bonding of the detached groups to form stable compounds. For example, according to a calculation[30] the interaction of *tert*-butyl cations with ROH in the presence of a proton acceptor (ammonia) takes place through the breaking of the O–H bond (not the C–O bond). When phenols are used the fragmentation along the O–H bond in the cationic polymerisation of isobutene[30] is favoured by the H-acidity, which is higher than in aliphatic alcohols, and by the p_π-p_π conjugation of the oxygen atoms with the aromatic nucleus, which suppresses the breaking of the bond between the aromatic carbon and the oxygen.

It follows from the calculations on the complexes of Lewis acids (R_nAlCl_{3-n}) with alcohols that the fragmentation of the alcohols by either of the possible directions (H^+ or R^+) has comparable probabilities. This conclusion is confirmed by experimental results. For example, when diisobutene (which is polymerised with difficulty) is used as a nucleophilic acceptor the protonation of the olefin is accompanied by a parallel reaction with the carbo-cation of the alcohol.[31]

Therefore according to both experimental and calculated data the fragmentation of alcohols substituted at the α carbon atom in complexes with strong acids takes place along the C–O bond, with formation of carbonium ions (i.e. R^+ activity is displayed). Conversely, decreasing the acid strength of the complex former, and especially using alcohols with unbranched radicals, strengthens the H^+ activity.

III. Complexes based on magnesium chlorides

The complexes of the magnesium chlorides with proton donors $R_nMgCl_{2-n} \cdot n_1 H_2O$ (n = 0–2; n_1 = 1, 2, 4, 6, 8, 12; R = OH, CH_3, C_2H_5, *iso*-C_3H_7, *tert*-C_4H_9) have a low activity towards the polymerisation of olefins, but nevertheless they allow us to prepare (under comparable conditions) a polymer having a molecular mass higher than would be obtained with other electrophilic initiating systems.[22]

1. Complexes based on magnesium chlorides and water

The values of the universal acidity indicator δpK_a and the charges on the hydrogen atom of the proton donor in the compounds of magnesium with H_2O are shown in Table 6.

Table 6. Acid strength of the aqua complexes $R_nMgCl_{2-n} \cdot n_1 H_2O$ (R = CH_3, C_2H_5, *iso*-C_3H_7, *tert*-C_4H_9).[10,32]

Aqua complex	q_{H^+}	δpK_a
H_2O	+0.140	+15.7
$H_2O \cdot MgCl_2$	+0.194	+7.1
$2\,H_2O \cdot MgCl_2$	+0.185	+7.7
$4\,H_2O \cdot MgCl_2$	+0.165	+10
$6\,H_2O \cdot MgCl_2$	+0.160	+14.4
$8\,H_2O \cdot MgCl_2$	+0.160	+14.4
$12\,H_2O \cdot MgCl_2$	+0.150	+15.1
$H_2O \cdot RMgCl$	+0.175 ± 0.005	+8.1 to +10
$2\,H_2O \cdot RMgCl$	+0.175 ± 0.005	+8.5 to +10
$H_2O \cdot R_2Mg$	+0.175 ± 0.005	+8.5 to +10
$2\,H_2O \cdot R_2Mg$	+0.175 ± 0.005	+8.5 to +10

The aqua complexes of the magnesium chlorides are characterised by high negative values of the overall energy of the system. These features are responsible for their stability and for the high energy of complex formation [E = −265 to −167 kJ mol^{-1}].

Irrespective of the nature of the ligands surrounding the magnesium the aqua complexes $R_nMgCl_{2-n} \cdot H_2O$ have a low Brønsted acidity (δpK_a = +7.1 to +15.1). The highest acid strength is found in the complexes $MgCl_2 \cdot H_2O$ (δpK_a = +7.1) and $MgCl_2 \cdot 2\,H_2O$ (δpK_a = +7.7), which suggests a high activity as catalysts for the polymerisation of isobutene.[22] However, the acid strength alone cannot account for the electrophilic properties of these complexes. It should not be forgotten that the geometry and the electronic structure of the $MgCl_2 \cdot H_2O$ aqua complexes are determined by the unusual type of coordination[10] of the H_2O to the $MgCl_2$. Under these conditions the size of the $MgCl_2 \cdot H_2O$ aqua complex (0.7–0.8 nm) increases in comparison with the $(CH_3)_2Mg \cdot H_2O$ aqua complex (0.3–0.4 nm).[9] Kennedy[22] came to the same conclusion. The polymerisation of isobutene under the influence of $MgCl_2$ takes place only in the presence of water and is associated with the complex nature of

Table 7. Characteristics of the $MgCl_2 \cdot n_1 H_2O$ complexes and some kinetic parameters of the thermocatalytic selective degradation of polyisobutene ($\overline{M}_n^0 = 5.75 \times 10^5$) and of butyl rubber ($\overline{M}_n^0 = 3.2 \times 10^5$) for $[MgCl_2 \cdot n_1 H_2O] = 1$ mol dm^{-3} (see Ref. 32).

Temperature/K	Conversion/mass %		Yield of isobutene/vol. %		$z \pm 10\%$		$10\,\upsilon\,(\pm 5\%)$/mol IB dm^{-3}		$10\,\upsilon_i\,(\pm 12\%)$/mol IB dm^{-3}	
	PIB	BR	PIB	BR	PIB	BR	PIB	BR	PIB	BR
Catalyst $MgCl_2 \cdot n H_2O$ ($n = 1, 2$)										
583	1.1	15.4	–	95.5	4.0	6.0	0.8	2.4	0.2	0.4
603	8.5	25.0	78.3	96.8	2.5	5.5	3.6	9.0	1.4	1.6
623	36.2	48.2	84.5	97.0	2.5	3.8	10.0	15.3	4.0	4.0
583	12.4	27.4	96.2	96.0	9.9	88.3	6.5	14.0	0.7	0.2
603	81.9	92.0	99.5	96.4	8.1	68.0	13.4	25.0	1.7	0.4
623	100.0	100.0	99.5	97.0	7.1	48.0	29.8	35.0	4.2	0.8
Catalyst $MgCl_2 \cdot 4 H_2O$										
583	11.4	19.7	90.1	93.1	9.4	72.0	6.5	7.7	0.7	0.1
603	36.2	31.6	92.4	92.0	6.8	70.0	12.4	14.5	1.8	0.2
623	62.0	35.9	98.6	97.0	–	56.0	–	20.4	–	0.4

Notes. υ is the rate of the reaction; υ_i is the rate of initiation.

the catalyst. The polymerisation requires the participation of growing carbonium ions, and the electric conductivity of the system is due to the presence of large complex counterions which may be incorporated in the solid phase. In the $MgCl_2 \cdot n_1 H_2O$ series of aqua complexes, with $n_1 = 4$, 6, 8 and 12, the energy of complex formation decreases, the charge on the hydrogen atom q_{H^+} decreases from 0.20 to 0.15, and δpK_a increases from +7.3 to +15.1. The charges on the hydrogen atoms in the water molecule, the energies of complex formation, and the δpK_a values in $RMgCl \cdot H_2O$ and $R_2Mg \cdot H_2O$ are effectively independent of the nature of the ligand surroundings of the magnesium. Similar results were obtained for the $R_2Mg \cdot 2H_2O$ and $R_2MgCl \cdot 2H_2O$ complexes.

Because of the low acid strength of the aqua complexes based on the magnesium chlorides (see Table 6), for example when used as catalysts for the electrophilic polymerisation of olefins, it is reasonable to suggest that the initiation stage of the process can be affected by the reacting bases (in particular, by the monomer molecules). An experimental confirmation of the views outlined above is provided by data obtained in studies of the electrophilic depolymerisation of isobutene polymers (PIB) and of butyl rubber (BR), containing ~1.6% of isoprene units, in the presence of $MgCl_2 \cdot n_1 H_2O$ (Table 7). We find a substantial (7-fold) decrease in the total yield of degradation products of PIB in the hydrogenation of the C=C end bonds. Because of the predominance of reactions proceeding by the 'laws of chance' over reactions proceeding by the 'law of end groups' (depolymerisation) in the degradation of polymers, the length of the kinetic chain z in the selective degradation of PIB and BR is much less than the length of the material chain $\overline{P}_n^0$. The lengths of the kinetic chain and the rates of initiation in the depolymerisation of PIB are commensurate with the values of these parameters in the purely thermal polymer degradation process. The presence of a second water molecule in $MgCl_2 \cdot 2H_2O$ (in contrast to $MgCl_2 \cdot H_2O$) has no effect on the rate of depolymerisation of PIB and BR, since the temperature of the transition of the dihydrate $MgCl_2 \cdot 2H_2O$ to the monohydrate $MgCl_2 \cdot H_2O$ (515 K) lies below the reaction temperature (523–623 K). The decrease in the positive charge in the series of magnesium aqua complexes ($MgCl_2 \cdot n_1 H_2O$) results in a marked decrease in the conversion of PIB into BR.[31,32]

These results show that the activity of the $MgCl_2 \cdot n_1 H_2O$ complexes in electrophilic processes, and in particular in the thermocatalytic selective degradation of PIB and BR, is due to their low acid strength.

2. Complexes based on magnesium chlorides and alcohols

The quantum chemical characteristics of the magnesium complexes $R_nMgCl_{2-n} \cdot ROH$ are shown in Table 8. Models of the complexes of alcohols with the magnesium haldies have been proposed by Sangalov et al.[10] To simplify the analysis all the models are divided into nine groups, depending on the nature of the ligand surroundings of the magnesium and on the extent of branching of the radical in the alcohol molecule. Aqua complexes of this type are characterised by high negative values of the total energy, which ensures the stability of catalysts based on complexes of alcohols with magnesium halides. The energy of formation of these complexes is quite high. The possibility of forming $R'_nMgCl_{2-n} \cdot ROH$ donor-acceptor complexes has been confirmed by quantum-chemical calculations (see Table 8).[10] Irrespectively of the nature of the substituents on the magnesium atom the complexes of magnesium halides with alcohols are characterised by a low Brønsted acidity ($\delta pK_a = +7.1$ to +12.0). The increase in δpK_a in the series CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH is dictated by the chemical structure of the compounds.

In the case of methanol the values of P_{OH} and P_{OC} for the R'_nMgCl_{2-n} complexes suggest a predominantly proton-donor activity, but with isopropanol (and, especially, *tert*-butanol) a carbo-cation activity is found. The $R'_nMgCl_{2-n} \cdot C_2H_5OH$ complexes can show H^+ and R^+ activities with equal probability.

To conclude this section we should note that irrespective of the ligand surroundings the acid strength of the complexes based on the magnesium chlorides and alcohols is relatively small (as it is with the $R'_nMgCl_{2-n} \cdot n_1 H_2O$ complexes). It follows that H^+ or R^+ activity can be displayed only through the direct participation of the reacting bases (olefins, arenes) in the initiation stage of the electrophilic polymerisation process.

IV. Complexes based on boron fluorides

Published reports of quantum-chemical calculations on complex cation-active centres of the type H^+, $[BF_4]^-$; H^+, $[BF_3 \cdot OH]^-$; R^+, $[BF_3 \cdot OH]^-$, and R^+, $[BF_3 \cdot OR]^-$ are not very abundant.[9,22,33–36] H^+ activity of the alcohols has been observed in compositions of the $BF_3 \cdot ROH$ complexes with R = CH_3, C_2H_5, n-C_3H_7, *iso*-C_3H_7, and others during the oligomerisation and polymerisation of propene, isobutene, and but-2-ene, and also in the alkylation of phenols by olefins.[37–39] However, the arguments put forward in support of H^+ initiation, such as the tenfold increase in the rate of polymerisation of styrene under the influence of $BF_3 \cdot C_2H_5OH$ as compared with the rate of the same reaction in the presence of $BF_3 \cdot O(C_2H_5)_2$ (see Refs 39 and 40) are not fully convincing. For this reason the formulae given to the electrophilic complex catalysts of the R^+, $[BF_3 \cdot OR]^-$ and H^+, $[BF_3 \cdot OH]^-$ type, widely used for the initiation of electrophilic reactions by the hydrates and etherates of boron trifluoride, are only hypothetical (though apparently reasonable).

Table 8. Quantum chemical parameters of the $ROH \cdot R_nMgCl_{2-n}$ models ($n = 0-2$; R = CH_3, C_2H_5, *iso*-C_3H_7, *tert*-C_4H_9).

Model No.	Model	Group	q_{H^+}	δpK_a	P_{OH}	P_{OC}	Activity type
1–4	$ROH \cdot MgCl_2$	I	0.20, 0.20, 0.19, 0.17	7.5, 7.5, 7.7, 12.0	0.93, 0.93, 0.93, 0.94	0.99, 0.93, 0.90, 0.89	H^+, H^+-R^+, R^+, R^+
5–8	$ROH \cdot CH_3MgCl$	II	0.20, 0.19, 0.19, 0.17	7.5, 7.7, 7.7, 12.0	0.94, 0.94, 0.94, 0.93	0.98, 0.94, 0.91, 0.91	H^+, H^+-R^+, R^+, R^+
9–12	$ROH \cdot (CH_3)_2Mg$	III	0.20, 0.19, 0.18, 0.18	7.5, 7.7, 8.5, 8.5	0.96, 0.94, 0.94, 0.93	0.97, 0.95, 0.91, 0.90	H^+-R^+, H^+-R^+, R^+, R^+
13–16	$ROH \cdot C_2H_5MgCl$	IV	0.20, 0.19, 0.18, 0.17	7.5, 7.7, 8.5, 12.0	0.93, 0.94, 0.93, 0.93	0.99, 0.93, 0.90, 0.89	H^+, H^+-R^+, R^+, R^+
17–20	$ROH \cdot (C_2H_5)_2Mg$	V	0.20, 0.19, 0.18, 0.17	7.5, 7.7, 8.5, 12.0	0.93, 0.93, 0.94, 0.93	1.0, 0.93, 0.91, 0.90	H^+, H^+-R^+, R^+, R^+
21–24	$ROH \cdot C_3H_7MgCl$	VI	0.19, 0.18, 0.18, 0.17	7.7, 8.5, 8.5, 12.0	0.92, 0.93, 0.93, 0.93	0.98, 0.94, 0.90, 0.90	H^+, H^+-R^+, R^+, R^+
25–28	$ROH \cdot (C_3H_7)_2Mg$	VII	0.20, 0.19, 0.17, 0.17	7.5, 7.7, 12.0, 12.0	0.93, 0.94, 0.93, 0.94	0.99, 0.94, 0.92, 0.89	H^+, H^+-R^+, H^+-R^+, R^+
29–32	$ROH \cdot C_4H_9MgCl$	VIII	0.20, 0.20, 0.19, 0.18	7.5, 7.5, 7.7, 8.5	0.94, 0.94, 0.94, 0.94	0.99, 0.93, 0.90, 0.89	H^+, H^+-R^+, R^+, R^+
33–36	$ROH \cdot (C_4H_9)_2Mg$	IX	0.20, 0.20, 0.18, 0.17	7.5, 7.5, 8.5, 12.0	0.92, 0.94, 0.94, 0.93	0.98, 0.95, 0.91, 0.90	H^+, H^+-R^+, R^+, R^+

Notes. Here and in Table 10 the sequence of numbers and symbols in the columns corresponds to the alcohols series with R = CH_3, C_2H_5, *iso*-C_3H_7, *tert*-C_4H_9; the following symbols are used: H^+ denotes a dominant proton-donor activity, R^+ denotes a dominant carbo-cation activity, H^+-R^+ states that the activities have equal probabilities.

1. Complexes based on boron fluorides and hydrogen fluoride

The quantum-chemical characteristics of the acid strength of the $R_nBF_{3-n} \cdot HF$ complexes are shown in Table 9. The structures calculated for the complexes based on the boron fluorides and hydrogen fluoride are distorted tetrahedra, similar to the structures of HBF_4 and $H_3O \cdot BF_4$ (see Eizner and Erusalimskii[9]). The very high positive charge concentrated on the hydrogen atoms (the proton donors) is surprising. The numerical values of the charges on the hydrogen atoms, $q_{H^+} = +0.48$ to $+0.50$, correspond to very low values of δpK_a. Therefore, according to Olah,[1] the complexes based on R_nBF_{3-n} and HF have 'superacid' properties. As in the case of the complexes based on the aluminium chlorides with strong proton donors ($R_nAlCl_{3-n} \cdot HCl$) the acidity of $RBF_{4-n} \cdot HF$ is independent of the nature of the ligand surroundings of the heteroatom.

Table 9. Acid strength of the complexes based on boron fluorides $R_nBF_{3-n} \cdot HF$ and $R_nBF_{3-n} \cdot H_2O$.

Complex	q_{H^+}	δpK_a
$HF \cdot BF_3$	+0.50	−60
$HF \cdot CH_3BF_2$	+0.49	−59
$HF \cdot (CH_3)_2BF$	+0.49	−59
$HF \cdot (CH_3)_3B$	+0.48	−58
$HF \cdot C_2H_5BF_2$	+0.49	−59
$HF \cdot (C_2H_5)_2BF$	+0.48	−58
$HF \cdot (C_2H_5)_3B$	+0.48	−58
$H_2O \cdot BF_3$	+0.23	+1.5
$H_2O \cdot CH_3BF_2$	+0.22	+4.4
$H_2O \cdot (CH_3)_2BF$	+0.22	+4.4
$H_2O \cdot (CH_3)_3B$	+0.21	+7.1
$H_2O \cdot F_4B_2O$	+0.24	+1.0

The removal of a proton H^+ is energetically favourable and offers a gain in energy of more than 350 kJ mol^{-1}. These electron-energy characteristics do not indicate the preliminary formation of a complex between HF and R_nBF_{3-n}, leading to the formation of stronger Lewis acids: rather, they suggest a preferential direct initiation of the cationic polymerisation of olefins by the scheme

$$HF + R_nBF_{3-n} \rightleftharpoons H^{\delta+}, [R_nBF_{4-n}]^{\delta-} \xrightarrow{M} HM^+, [R_nBF_{3-n}]^-.$$

Therefore the consensus of the quantum-chemical calculations and of the experimental data points to an ordinary, classical H^+ initiation mechanism for the electrophilic polymerisation process in the presence of complexes of boron fluoride with proton donors.

2. Complexes based on boron fluorides and water

The aqua complexes $R_nBF_{3-n} \cdot H_2O$ are characterised by high negative values of the total energy and of the overall energy of the bonds, which ensure the stability of the complexes. Additional evidence of the donor–acceptor nature of the complexes based the boron fluorides and water has been provided by data[10] on their geometry and on their electron-energy characteristics. The parameters of the acid strength of $R_nBF_{3-n} \cdot H_2O$ (q_{H^+} and δpK_a) show that these complexes have a low acidity irrespective of the chemical nature of the ligand surroundings of the heteroatom. However, the aqua complexes of the $R_nBF_{3-n} \cdot H_2O$ type have a slightly greater acid strength than the aqua complexes based on the chlorides of magnesium and aluminium. This corresponds to well known experimental data on the greater activity and slightly lower selectivity of the $R_nBF_{3-n} \cdot H_2O$ as compared with $R_nAlCl_{3-n} \cdot H_2O$ complexes in the cationic polymerisation of olefins.[13,23] The spontaneous protonation of the compound $R_nBF_{3-n} \cdot H_2O$ is effectively impossible because the removal of a proton requires an expenditure of energy of more than 150 kJ mol^{-1}. Therefore even in the aqua complexes of the boron fluorides the appearance of proton-donor activity is determined by the acceptor function of the base (olefin, arene, etc.).

3. Complexes based on boron fluorides and alcohols

Quantum-chemical calculations for the complexes $R'_nBF_{3-n} \cdot ROH$, analogous to the calculations for $R'_nAlCl_{3-n} \cdot ROH$ and $R'_nMgCl_{2-n} \cdot ROH$, have established the mutual dependence of their electrophilicity and of the appearance of proton-donor (as opposed to carbo-cation) activity.

Table 10. Quantum chemical parameters of the ROH · R_nBF_{3-n} · ROH complexes (n = 0–3; R = CH_3, C_2H_5, *iso*-C_3H_7, *tert*-C_4H_9).

Model No.	Complex	Group	q_{H^+}	δpK_a	P_{OH}	P_{OC}	Activity type
1–4	ROH · BF_3	I	0.24, 0.23, 0.21, 0.21	1.0, 1.5, 7.1, 7.1	0.92, 0.92, 0.92, 0.92	0.98, 0.97, 0.94, 0.94	H^+, H^+, H^+-R^+, R^+
5–8	ROH · CH_3BF_2	II	0.23, 0.22, 0.20, 0.19	1.5, 4.4, 7.3, 7.7	0.92, 0.92, 0.93, 0.93	1.01, 0.96, 0.90, 0.89	H^+, H^+, R^+, R^+
9–12	ROH · $(CH_3)_2BF$	III	0.23, 0.21, 0.20, 0.20	1.5, 7.1, 7.3, 7.3	0.92, 0.94, 0.92, 0.93	1.0, 0.97, 0.94, 0.90	H^+, H^+, H^+-R^+, R^+
13–16	ROH · $(CH_3)_3B$	IV	0.24, 0.23, 0.22, 0.20	1.0, 1.5, 4.4, 7.3	0.94, 0.92, 0.94, 0.92	0.96, 0.95, 0.91, 0.89	H^+-R^+, H^+, R^+, R^+
17–20	ROH · $C_2H_5BF_2$	V	0.23, 0.22, 0.22, 0.20	1.5, 4.4, 4.4, 7.1	0.93, 0.92, 0.94, 0.93	0.98, 0.96, 0.93, 0.89	H^+, H^+, H^+-R^+, R^+
21–24	ROH · $(C_2H_5)_2BF$	VI	0.24, 0.23, 0.21, 0.20	1.0, 1.5, 7.1, 7.3	0.92, 0.92, 0.92, 0.93	0.97, 0.95, 0.93, 0.90	H^+, H^+, H^+-R^+, R^+
25–28	ROH · $(C_2H_5)_3B$	VII	0.22, 0.21, 0.21, 0.20	4.4, 7.1, 7.1, 7.3	0.92, 0.93, 0.92, 0.93	0.90, 0.95, 0.93, 0.90	H^+, H^+-R^+, H^+-R^+, R^+
29–32	ROH · $C_3H_7BF_2$	VIII	0.23, 0.22, 0.20, 0.20	1.5, 4.4, 7.3, 7.3	0.92, 0.93, 0.92, 0.92	0.98, 0.97, 0.93, 0.89	H^+, H^+, H^+-R^+, R^+
33–36	ROH · $(C_3H_7)_2BF$	IX	0.24, 0.24, 0.21, 0.20	1.0, 1.0, 7.1, 7.3	0.92, 0.93, 0.93, 0.92	0.99, 0.96, 0.94, 0.89	H^+, H^+, H^+-R^+, R^+
37–40	ROH · $(C_3H_7)_3B$	X	0.22, 0.22, 0.21, 0.19	4.4, 4.4, 7.1, 7.7	0.92, 0.92, 0.92, 0.92	0.99, 0.96, 0.93, 0.89	H^+, H^+, H^+-R^+, R^+
41–44	ROH · $C_4H_9BF_2$	XI	0.23, 0.21, 0.21, 0.20	1.5, 7.1, 7.1, 7.3	0.92, 0.93, 0.92, 0.92	0.99, 0.96, 0.93, 0.89	H^+, H^+, H^+-R^+, R^+
45–48	ROH · $(C_4H_9)_2BF$	XII	0.23, 0.22,	1.5, 4.4,	0.92, 0.93,	1.0, 0.97,	H^+, H^+,

A detailed collection of the quantum-mechanical evidence for the existence of the R'_nBF_{3-n} · ROH (electronic structure, geometry) has been published.[10] The charges on the hydrogen atoms of the alcohol, which are well correlated with the values of the universal acidity indicator, and the predominant type of activity of the alcohol are listed in Table 10. In all 13 groups the positive charge on the hydrogen atom in the complexes based on boron fluorides and alcohols decreases as the branching of the radical in the molecule is increased. Therefore the q_{H^+} values are independent of the ligand surroundings of the heteroatom, and are determined by the chemical structure of the radical in the ROH molecule. The acid strength of the R'_nBF_{3-n} · ROH complexes decreases in the alcohol series methanol > ethanol > > isopropanol > *tert*-butanol, but the P_{OH} bond orders remain practically unchanged for all 52 models of the alcohol–boron fluoride complexes. The P_{OC} bond order tends to decrease when the acidity indicator of the complexes δpK_a is lowered. The complexes of CH_3OH and C_2H_5OH with the boron fluorides show preferentially H^+ activity. When isopropanol is used the proton-donor and the carbo-cation activity appear with equal probabilities. Alternative possibilities for the fragmentation of the alcohol molecules in the complexes with boron fluorides have been identified experimentally[25,37–40] is a function of the chemical structure of the alcohol residue R.

Thus the R'_nBF_{3-n} · ROH complexes are characterised by a low Brønsted acidity irrespective of the nature of the ligands. The development of proton-donor or of carbo-cation activity in the alcohols is determined by the chemical structure of the radical in the alcohol molecule, and is associated with the direct participation of bases in the polymerisation reactions of the olefins (in particular, molecules of the monomer, of the aromatic solvent, etc.).

V. Conclusions

The accumulated fund of experimental data on the acid strength and catalytic activity of adequately stable complexes consisting of the halides, alkyls, and alkyl halides of the nontransition metals (Al, B, Mg) and of proton donors (H_2O, ROH, HCl, HF) in electrophilic polymerisation processes, in conjunction with corresponding quantum-chemical calculations, justify the conclusion that the acid strength of the proton donors in these complexes is a measure of the activity and selectivity of their action as catalysts in electrophilic reactions. Important new information has been acquired, offering a deeper understanding of the role of the acid strength of these complexes in electrophilic polymerisation processes.

1. Complexes of the R_nAlCl_{3-n} · HCl and R_nBF_{3-n} · HF type have a high acid strength, independent of the ligand surroundings of the heteroatom (Al, B) ($\delta pK_a = -16$ to -60). The removal of a proton is energetically favourable. The complexes undergo spontaneous ionisation and can initiate electrophilic polymerisation.

2. Complexes of the R_nAlCl_{3-n} · H_2O, R_nMgCl_{2-n} · H_2O, and R_nBF_{3-n} · H_2O type, and products of their transformation ($HOAlCl_2$ · H_2O, Al_2Cl_4O · H_2O, R_nAlCl_{3-n} · H_2O · HCl, etc.), have a low acid strength ($\delta pK_a = +1.3$ to $+14.4$). The removal of a proton is energetically unfavourable. Complexes of this type are not prone to spontaneous ionisation, and they can initiate electrophilic polymerisation in the presence of weak bases.

3. Complexes of the R'_nAlCl_{3-n} · ROH, R'_nMgCl_{2-n} · ROH, and R'_nBF_{3-n} · ROH type are characterised (like the corresponding aqua complexes) by a small acid strength ($\delta pK_a = +1.0$ to $+15.1$). The removal of a proton is energetically unfavourable. Complexes of this type do not undergo spontaneous ionisation. Depending on the chemical structure of the radical R in the alcohol molecule, on the acid strength of the complex former, and (if the acid strength is low) on the specific interactions of the reactants, and also depending on the special features of the coordination of the proton donors (H_2O, ROH) with the Lewis acids (mainly, magnesium compounds), the alcohol molecules bound in complexes can display either a proton activity or a carbo-cation activity. In the electrophilic polymerisation of olefins this effect influences the initiation stage, and therefore also the character of the end groups in the resulting macromolecules. Increasing the size of the ligand in the Lewis acid (see Table 2) or the volume of the

radical R in the alcohol molecules (see Table 4) included in the composition of complexes of nontransition metal halides with proton donors increases the selectivity of the polymerisation.

Thus the complexes of the halides of nontransition metals with weak proton donors (H_2O, ROH) have a low acid strength, which casts doubts on the ability of these materials to show a catalytic activity in electrophilic processes, and a weak dependence of the acid strength on the chemical nature of the initial Lewis acid. In this case the role of the monomer as an electron donor and its direct participation in the formation of active centres become the dominant factors.[41]

The method of calculating the acid strength of the complex catalysts in the R_nAlCl_{3-n}–proton-donor system[41–43] can be extended to a wider class of complexes based on the halides of nontransition metals (B, Mg, etc.) and on proton donors (H_2O, ROH, HCl, HF, etc.). The method is convenient and promising for calculating the acid strength of newly synthesised H complexes in order to predict their catalytic activity and selectivity in electrophilic processes. The acidity parameters q_{H^+} obtained in this way by calculations on appropriate models of the complex catalysts are expressed in the form of δpK_a by using a well known correlation expression.[6] An analysis of the acidity of more than 300 compounds and complexes thought to be potential catalysts for electrophilic polymerisation processes in olefins identified the following ranges of δpK_a values (see Fig. 2):

from +50 to +12 (very low values); complexes having these acidities show no catalytic activity towards electrophilic polymerisation processes (the individual compounds ROH and H_2O, and also $AlR_3 \cdot H_2O$, $AlR_3 \cdot ROH$, etc., see Tables 3, 5, and 6);

from +12 to +1 (optimum values); catalysts having these acidities have a high activity and selectivity ($C_2H_5Cl_2Al \cdot H_2O$, $AlCl_3 \cdot H_2O$, $MgCl_2 \cdot H_2O$, $C_2H_5AlCl_2 \cdot ROH$ etc., see Tables 3, 5, 6);

from +1 to −60 (high values); at these acidities the H complexes are much more active, but very much less selective ($R_nAlCl_{3-n} \cdot HCl$, $R_nBF_{3-n} \cdot HF$, protonated alcohols, see Tables 1 and 2).

We may conclude from the above that increasing the acid strength of electrophilic polymerisation catalysts increases the activity of the catalysts but lowers the selectivity of the process.

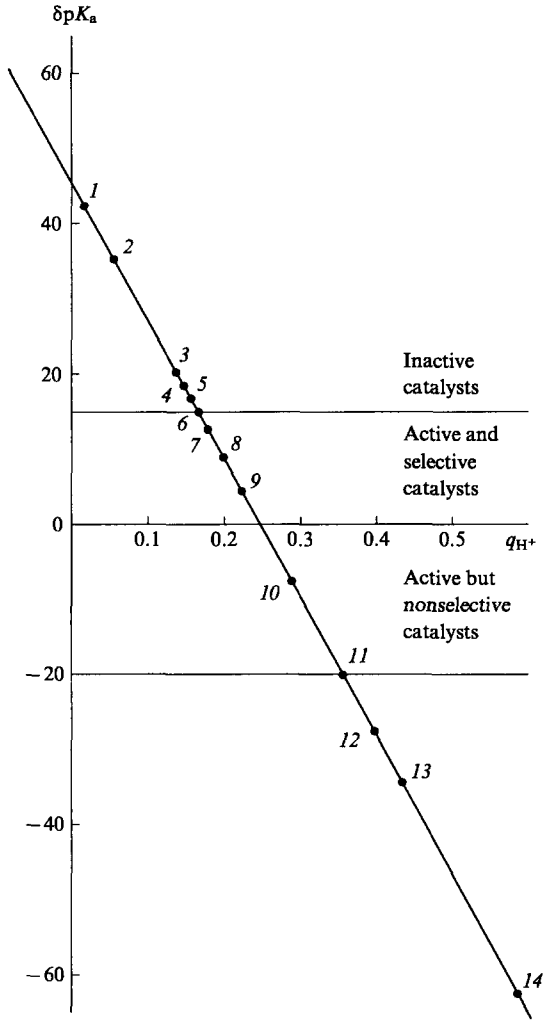


Figure 2. Relationship between the universal acidity indicator and the charge on the hydrogen atom.[6,41]

(*1*) CH_4; (*2*) NH_4^+;
(*3*) $(CH_3)_3COH$; (*4*) CH_3OH;
(*5*) $H_2O \cdot R_2AlCl$, $H_2O \cdot R_3Al$; (*6*) H_2O;
(*7*) $Si(OH)_4$; (*8*) $H_2O(ROH) \cdot AlRCl_2 \cdot (R_nMgCl_{2-n})$;
(*9*) $H_2O \cdot Al_2Cl_4OH$; (*10*) $(CH_3)_3C^+ \cdot HOC_2H_5$;
(*11*) $H_3C^+ \cdot HOC_2H_5$; (*12*) $H_3C^+ \cdot CH_3OH$;
(*13*) $H^+ \cdot CH_3OH$; (*14*) $HF \cdot R_nBF_{3-n}$.

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