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Complexes of metal chlorides with proton donors — promising polyfunctional catalysts for electrophilic processes

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Abstract. The Brønsted acids formed as a result of the interaction of aluminium chlorides with Group I and II metal chlorides in the presence of proton-donating compounds are promising polyfunctional catalysts for electrophilic processes (polymerisation, depolymerisation and degradation of macromolecules, alkylation, desulfurisation, and hydrogenation). The factor determining the electrophilic activity and selectivity of the action of the catalysts is their acidity. This makes it possible to predict the direction of the changes in the activity and selectivity of the catalyst in specific chemical processes in conformity with the opposite variation rule: with increase in the acidity of the electrophilic catalyst, their activity increases but the selectivity of their action diminishes. The bibliography includes 72 references.

I. Introduction

The importance of catalysis in modern chemistry, characterised by the diversity of reactions, the enormous number of compounds, and the possibility of their modification, is very great. Naturally, the search for readily available active and selective combined-action catalysts, which make it possible to achieve under mild conditions many chemical reactions of practical importance and to investigate their properties, is of special interest.

The classical catalysts based on metal chlorides, used in numerous electrophilic reactions, are $AlCl_3$, $FeCl_3$, $SnCl_4$, etc. However, their high relative acidity also when they are combined with cocatalysts (H_2O, CH_3Cl, HCl, etc.) (Table 1, see over) is responsible in many instances for the occurrence simultaneously with the main process of undesirable chemical reactions (side and secondary reactions), such as the decomposition of the catalytic system, tar and coke formation, degradation of molecules, cross-linking of macrochains, etc. On the other hand, for catalysts characterised by a low acidity the very manifestation by the latter of catalytic properties is doubtful. It is therefore useful to consider the catalytic properties of metal chloride complexes with an acidity lower than that of $AlCl_3$, $SnCl_4$, etc. In particular, a relation between the acidity of electrophilic catalysts and their catalytic activity[6–16] and also the selectivity of their action[13–17] has been noted. The acidity of electrophilic catalysts has therefore attracted attention as a possible criterion for the preliminary assessment of their postulated activity and selectivity.

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II. Cationic polymerisation of alkenes

The complexes of aluminium chlorides with proton-donating compounds, i.e. $H[AlCl_3OH]$, $H[Al(C_2H_5)Cl_2OH]$, etc., are catalysts for electrophilic oligo-, poly-, and co-polymerisation reactions of alkenes.[10–13,18,19] By varying the chemical nature of the Lewis acid and the proton donor (H_2O, ROH, HCl, etc.) and in essence the parameters of the acid strength of the catalyst, it is possible to form complexes with a wide range of activities and selectivities † of their action (Table 2, see over).[2,17,20,21]

The ability of electrophilic catalysts to initiate the process is determined by their acid properties, since cationic polymerisation constitutes an unusual sequence of steps occurring in accordance with the principle of the neutralisation of an acid (the active centre) by a base (the monomer),[22,23] and one has to bear in mind that, in the initiation of polymerisation by H acids, the highly acid protons abolish to some extent the differences between the basicities of the alkene monomers and, conversely, weakly acid centres are distinguished by enhanced selectivity in relation to them. The cause of the low selectivity of strongly acid (hard) centres ($H^{\delta+}$), of 'superstrong' acids is that they can interact with single C–C bonds, inducing their dissociation.[24]

The data presented below[10,25] confirm the conclusion that the activity of 'Lewis acid–cocatalyst' complex systems in the electrophilic polymerisation of alkenes depends on their acidity. For clarity, the 'Lewis acid–electron-donating

† Here and henceforth, the degree of conversion of the reactant (%) has been adopted as a measure of the activity of the catalyst.

Table 1. Acidity indices of electrophilic catalysts based on metal chlorides.

Catalyst	RAI/mequiv. (g cat.)$^{-1}$ (±0.1)	pK_a (±0.1)	q_{H^+} (±0.02)	Catalyst	RAI/mequiv. (g cat.)$^{-1}$ (±0.1)	pK_a (±0.1)	q_{H^+} (±0.02)
$H[AlCl_3OH]$	5.0	−22	0.45	$H[CdCl_2OH]$	0.1	+17.8	0.10
$H[AlCl_4]$	4.4	−16	—	$H[Al(C_2H_5)Cl_3]$	4.3	−16	—
$H[FeCl_2OH]$	3.5	−10	0.34	$H[MgAlCl_5OH]$	2.3	0	0.24
$H[BiCl_3OH]$	2.8	−4.2	0.29	$H[MgAl(C_2H_5)Cl_4OH]$	2.2	+0.9	0.25
$H[InCl_3OH]$	2.6	−2.5	0.27	$H[CaAlCl_5OH]$	2.2	+0.9	0.25
$H[MgInCl_5OH]$	1.9	+3.5	0.21	$H[CaAl(C_2H_5)Cl_4OH]$	1.8	+4.0	0.21
$H[CaInCl_5OH]$	1.6	+4.5	0.22	$H[LiAl(C_2H_5)Cl_3OH]$	1.8	+4.1	0.18
$H[MgCl_2OH]$	1.5	+7.1	0.19	$H[Al_2Cl_4(O)OH]$	—	+4.4	0.21
$H[MgCl_2OH]\cdot H_2O$	1.5	+7.7	0.18	$H[NaAlCl_4OH]$	1.6	+4.5	0.23
$H[Mg(C_4H_9)ClOC_3H_7]$	—	+7.7	0.19	$H[SrAlCl_5OH]$	1.6	+5.0	0.21
$H[AlCl_3OC_2H_5]$	1.5	+7.7	0.19	$H[BaAl(C_2H_5)Cl_4OH]$	1.4	+7.3	0.18
$H[Mg(C_2H_5)ClOH]$	—	+8.1	0.17	$H[NaAl(C_2H_5)Cl_3OH]$	1.4	+7.2	0.19
$H[Mg(C_3H_7)ClOC_3H_7]$	—	+8.5	0.18	$H[Al(C_2H_5)Cl_2OH]$	—	+7.5	0.20
$H[MgCl_2OH]\cdot 3H_2O$	1.0	+10.5	0.16	$H[Al(C_2H_5)_2ClOH]$	—	+8.5	0.18
$H[CaCl_2OH]$	1.0	+10.5	0.16	$H[Al(OH)Cl_2OH]$	—	+8.5	0.18
$[MnCl_2OH]$	1.0	+10.5	0.16	$H[Al_2(CH_3)_3Cl(O)OH]$	—	+8.5	0.18
$H[BaCl_2OH]$	0.9	+11.6	0.15	$H[ZnAlCl_5OH]$	1.1	+9.8	0.16
$H[CoCl_2OH]$	0.6	+13.8	0.13	$H[CdAlCl_5OH]$	1.1	+9.8	0.16
$H[NiCl_2OH]$	0.5	+14.5	0.12	$H[KAlCl_4OH]$	0.9	+11.6	0.13
$H[ZnCl_2OH]$	0.2	+17.0	0.10	$H[KAl(C_2H_5)Cl_3OH]$	0.8	+12.0	0.13

Note. RAI is the relative acidity index (experiment);[1] pK_a is the universal acidity index;[2,3] q_{H^+} is the charge on the catalyst hydrogen atom (quantum-mechanical calculation).[2-5]

Table 2. Polymerisation of isobutene in a mixture of hydrocarbons in the presence of complexes of aluminium chlorides with proton-donating compounds.

Catalyst	Composition of initial mixture of hydrocarbons (mass %)				Degree of conversion of isobutene (mass %)	Selectivity with respect to isobutene (relative units)
	C_3H_8	C_4H_{10}	iso-C_4H_8	Σ(*n*-C_4H_8)		
$H[AlCl_4]\cdot AlCl_3$ [a]	0.6	55.1	14.9	29.5	99	0.3
$H[Al(C_2H_5)Cl_3]$ [a]	0.6	55.1	14.9	29.5	86	0.4
$H[Al(C_2H_5)_2Cl_2]$ [a]	0.6	55.1	14.9	29.5	98	0.6
$H[Al(C_2H_5)Cl_2OC(C_6H_5)_3]$	0.6	55.1	14.9	29.5	90	0.8
$H[Al(C_2H_5)Cl_2OCH_3]$	0.6	55.1	14.9	29.5	95	0.8
$H[Al(C_2H_5)Cl_2OH]$	0.9	45.1	31.1	23.0	99	1.0
$H[Al(C_2H_5)Cl_2OH]$	3.0	55.5	37.9	3.5	96	1.0
$H[Al(C_2H_5)Cl_2OH]$	3.9	67.5	11.3	17.3	98	1.0
$H[Al(C_2H_5)Cl_2OC(CH_3)_3]$	3.0	55.5	37.9	3.5	90	0.8

Note. Reaction conditions: T = 253 K, concentration of hydrocarbons 1.3 M, [Cat] = 5.6×10^{-2} M, solvent — heptane.
[a] [Cat] = 7.3×10^{-3} M, solvent — CH_2Cl_2.

additive' complexes are arranged in series in conformity with their electrophilic activity (the region of active systems is indicated).

$BF_3\cdot R_2O$	$\underline{AlCl_3\cdot R_2O}$	$RAlCl_2\cdot R_2O$	$R_2AlCl\cdot R_2O$	$R_3Al\cdot R_2O$
$BF_3\cdot ROH$	$AlCl_3\cdot ROH$	$\underline{RAlCl_2\cdot ROH}$	$R_2AlCl\cdot ROH$	$R_3Al\cdot ROH$
$BF_3\cdot H_2O$	$AlCl_3\cdot H_2O$	$RAlCl_2\cdot H_2O$	$\underline{R_2AlCl\cdot H_2O}$	$\underline{R_3Al\cdot H_2O}$
$BF_3\cdot HHal$	$AlCl_3\cdot HHal$	$RAlCl_2\cdot HHal$	$R_2AlCl\cdot HHal$	$R_3Al\cdot HHal$

The substituents R in the Lewis acid and in the electron-donating additive can be both the same and different.

With decrease in the strength of the Lewis acids from left to right, the set of activators from isotypical series promoting the formation of the active centres becomes narrower. The strongest acid (BF_3) induces the ionisation of all the activating bases.[26] Owing to their weak electron-accepting properties, weak Lewis acids show a low activity or are inactive. Evidently, the majority of the effective electrophilic catalysts occupy an intermediate position between the two cases examined as regards their activity.

Formal considerations[10,19] show that the mechanism of the cationic polymerisation of alkenes, in particular isobutene (IB), is fairly simple and includes the following elementary stages with participation of carbonium ions:

(a) the formation of the catalytic complex:

$$MCl_n + H_2O \longrightarrow [MCl_n\cdot H_2O] \longrightarrow H^{\delta+}, [MCl_nOH]^{\delta-} \text{ (or } H^+, A^-);$$

(b) initiation:

$$H^{\delta+}, [MCl_nOH]^{\delta-} + H_2C{=}C(CH_3)_2 \xrightarrow{k_i} (CH_3)_3C^{\delta+}, [MCl_nOH]^{\delta-};$$

(c) chain propagation:

$$(CH_3)_3C^{\delta+}, [MCl_nOH]^{\delta-} + H_2C=C(CH_3)_2 \xrightarrow{k_p}$$
$$\longrightarrow (CH_3)_3C-CH_2-\overset{\delta+}{C}(CH_3)_2, [MCl_nOH]^{\delta-} \text{ etc.};$$

(d) chain transfer to the monomer:

$$\sim CH_2-\overset{\delta+}{C}(CH_3)_2, [MCl_nOH]^{\delta-} + H_2C=C(CH_3)_2 \longrightarrow$$
$$\xrightarrow{k_m} \sim CH_2-C(=CH_2)(CH_3) + (CH_3)_3C^{\delta+}, A^{\delta-}$$
$$\xrightarrow{k_m} \sim CH=C(CH_3)_2 + (CH_3)_3C^{\delta+}, A^{\delta-};$$

(e) proton transfer to the counterion (probable reaction):

$$\sim CH_2-\overset{\delta+}{C}(CH_3)_2, [MCl_nOH]^{\delta-} \longrightarrow$$
$$\xrightarrow{k_{ci}} \sim CH_2-C(=CH_2)(CH_3) + H^{\delta+}, [MCl_nOH]^{\delta-}$$
$$\xrightarrow{k_{ci}} \sim CH=C(CH_3)_2 + H^{\delta+}, [MCl_nOH]^{\delta-};$$

(f) chain termination with capture of a fragment of the counterion.

$$\sim CH_2-\overset{\delta+}{C}(CH_3)_2, [MCl_nOH]^{\delta-} \longrightarrow$$
$$\xrightarrow{k_t} \sim CH_2C(CH_3)_2Cl + MCl_{n-1}OH$$
$$\xrightarrow{k_t} \sim CH_2C(CH_3)_2OH + MCl_n$$

Like the polymerisation of other alkenes, the polymerisation of isobutene has a series of characteristic features associated with the occurrence of reactions involving the formation and growth of polymeric carbonium ions. The slight internal stabilisation of the growing carbonium ions having the isobutene structure (owing to the absence of strong electron-donating substituents at the cationic centre) is responsible for the significant role of the solvating (electrostatic) function of the monomer despite its low relative permittivities ($\varepsilon = 2-3$). The low degree of solvation of carbonium ions by virtue of their size does not rule out but actually presupposes the effective external stabilisation of the cationic active centre by means of the monomer, associated with its nucleophilicity. This is the reason for the extremely rapid growth of carbonium ions, characteristic of the electrophilic polymerisation of isobutenes, such growth determining in its turn the characteristic features of the isobutene polymerisation reaction in the presence of metal chloride complexes with proton-donating compounds. As a consequence of the high rates of polymerisation and at the same time a fairly pronounced exothermicity of the process (71.9 kJ mol^{-1}), a situation arises such that, even for very slow addition of the initiator and rapid stirring, it is not possible to remove the heat evolved during the reaction in the liquid phase. In this case, the kinetic constants (in particular, $k_p > 10^6$ litre $mol\ s^{-1}$), especially under the conditions involving the formation of a viscous product, may prove to be higher than the diffusion constant (k_D) and the reaction begins almost immediately after the addition of drops of the initiator solution to the liquid monomer, i.e. long before the monomer and initiator drops have been mixed.[19] Hence it follows that, in the cationic polymerisation of isobutene in the presence of metal chloride complexes with proton-donating compounds and a series of other electrophilic catalysts, the principle of a steady-state process cannot be maintained. This means that in reality the molecular masses of the polymer are lower and the molecular distribution (MMD) is broader than expected for an isothermal process (this is in fact observed experimentally[27,28] under industrial conditions). Calculation for the nonstationary polymerisation of isobutene in turbulent streams and modelling of this process have been described in detail in a number of studies[29-35] and will not be discussed in the present review.

III. Degradation of polyalkenes (depolymerisation and degradation of macrochains)

Certain complexes of metal chlorides with a reduced acidity compared with $AlCl_3$, especially catalytic systems such as Brønsted acids based on double salts of aluminium chlorides with Group I and II metal chlorides and proton-donating compounds {H[MAlCl$_4$OH], H[MAlCl$_5$OH], H[MAl(R)Cl$_3$OH], etc.}, are extremely active in processes involving the selective *thermocatalytic degradation of polyalkenes, butyl rubber* (BR),[8-10,36-46] and petroleum raw material.[47-49] The main gaseous products are then C_4 hydrocarbons (Table 3, see over).

The purely thermal decomposition of polyalkenes is accompanied by the formation of a large set of reaction products (ranging from C_1 to C_6 hydrocarbons), characteristic of the pyrolysis of hydrocarbons. Therefore the concept of selectivity loses its significance when applied to the thermal degradation of polyalkenes.

The electrophilic catalytic degradation of polyalkenes in the presence of H[AlCl$_3$OH] proceeds with a higher yield of low-molecular-mass gaseous products than in the purely thermal decomposition and at lower temperatures. However, this reaction too is insufficiently selective judging from the yield of the monomer (Table 3), because the decomposition of polymeric carbonium ions in the presence of a relatively hard acid involves the formation of a series of gaseous products: ranging from CH_4 (abstraction of methyl substituents) to C_4H_{10} and C_4H_8 (skeletal isomerisation of the macroion with subsequent β-decomposition of the carbonium ion) and also of liquid and wax-like substances, in particular C_5 and other higher hydrocarbons. A major role is attributed in this case to reactions involving random chain transfer to the polymer. Thus the high acidity of the electrophilic polymerisation catalysts promotes an increase in their activity, but reduces the process selectivity. A moderate decrease in the acidity of catalysts of the type H[MAlCl$_4$OH] and H[MAlCl$_5$OH] (compared with $AlCl_3$, etc.) (Table 1) has a favourable effect on the relative contributions of the chain propagation and chain transfer reactions.[37,40] As a result, the process selectivity as regards the yield of C_4 hydrocarbons, in particular iso-C_4 hydrocarbons, increases appreciably (Table 3).

The mechanism of the thermocatalytic degradation of polyalkenes in the presence of catalysts with reduced acidity compared with $AlCl_3$—complexes of metal chlorides with proton donors—differs from the mechanism of the purely thermal decomposition reactions of the alkenes.

The thermolysis of polyalkenes proceeds via a free-radical mechanism,[50] whereas the degradation of polyalkenes in the presence of electrophilic catalysts, in particular Brønsted acids, takes place with participation of carbonium ions.[8,9,51-54]

It has been demonstrated experimentally and theoretically (the LCAO-MO method in the CNDO/2 approximation[8,9,46]) that proton-donating compounds participate in the formation of

Table 3. Thermocatalytic degradation of polyalkenes.

Catalyst	Yield of gaseous products (mass %)[a]	Composition of C_4 hydrocarbons (mass %)			Selectivity of catalyst (relative units)
		iso-C_4H_{10}	iso-C_4H_8	$\sum C_4$	
Polyethylene					
Without catalyst	41[b]	1.1	18.7	47.1	0.57
H[$AlCl_3OH$]	16.2	31.6	2.5	47.5	0.57
H[$LiAlCl_4OH$]	11.1	50.5	18.5	79.8	0.8
H[$NaAlCl_4OH$]	8.4	50.3	24.0	79.3	0.82
H[$KAlCl_4OH$]	3.0	41.7	25.9	83.9	0.85
H[$Li(C_2H_5)AlCl_3OH$]	10.2	39.2	26.5	83.4	0.85
H[$Na(C_2H_5)AlCl_3OH$]	7.0	38.4	27.3	89.8	0.9
H[$K(C_2H_5)AlCl_3OH$]	4.0	39.3	21.2	78.3	0.88
$MgCl_2 \cdot AlCl_3 \cdot H_2O$	88.2[c]	42.5	21.8	85.0	0.85
H[$Mg(C_2H_5)AlCl_4OH$]	54.0	39.9	28.2	89.3	0.89
H[$Ca(C_2H_5)AlCl_4OH$]	42.0	37.8	22.7	89.4	0.89
H[$Ba(C_2H_5)AlCl_4OH$]	31.0	37.3	24.3	91.3	0.9
Polyisobutylene					
Without catalyst	76.0[c]	2.1	16.0	19.1	0.2
H[$AlCl_3OH$]	63.0[c]	2.1	19.1	22.1	0.2
H[$NaAlCl_4OH$]	38.2	7.0	88.8	98.1	1.0
H[$Li(C_2H_5)AlCl_3OH$]	27.0	7.0	87.5	97.5	1.0
H[$Na(C_2H_5)AlCl_3OH$]	24.2	6.9	88.3	98.3	1.0
H[$K(C_2H_5)AlCl_3OH$]	19.8	7.2	87.3	97.8	1.0
$MgCl_2 \cdot AlCl_3 \cdot H_2O$	93.8	24.2	73.4	98.0	1.0
H[$Mg(C_2H_5)AlCl_4OH$]	59.6	7.0	91.3	99.1	1.0
H[$Ca(C_2H_5)AlCl_4OH$]	54.0	7.2	90.5	98.3	1.0
H[$Ba(C_2H_5)AlCl_4OH$]	45.2	8.1	86.5	98.6	1.0
Butyl rubber					
Without catalyst	50.5[c]	traces	3.0	36.7	0.6
H[$AlCl_3OH$]	75.0	58.3	0.5	58.8	0.6
H[$LiAlCl_4OH$]	39.8	23.6	39.1	76.1	0.75
H[$KAlCl_4OH$]	86.0	30.3	24.8	62.3	0.62
$MgCl_2 \cdot AlCl_3 \cdot H_2O$	75.4	2.1	93.8	97.2	1.0

Note. Reaction conditions: $T = 573$ K, process time 1 h, [Cat] = 1×10^{-3} mol g^{-1}, the values of $\bar{M}_n$ for high pressure polyethylene (HPPE), polyisobutylene (PIB), and butyl rubber (isobutene–isoprene copolymer, 1.7 mol.% of BR) are 2200, 1100, and 257 000 respectively. [a] Molecular hydrogen was identified among the gaseous products; [b] T = 673 K; [c] T = 653 K.

the electrophilic catalysts. The influence of H_2O and ROH in the activation of electrophiles is determined by the dissociative adsorption of such a proton-donating cocatalyst on the catalyst surface. Therefore the structure of the electrophilic centres corresponds to the structure of the Brønsted acid: $H^+[AlCl_3OH]^-$, $H^+[AlCl_3OR]^-$, $H^+[MAlCl_4OH]^-$, $H^+[MAl.(C_2H_5)Cl_3OH]^-$, etc. The series of changes in the activity of such catalysts is consistent with the increase in their acidity (Table 1). They are capable of initiating both the random decomposition of macromolecules (degradation of polymer chains) and their decomposition in accordance with the end group route (depolymerisation of polymer chains).[37,40] Depending on the type of process, particular reaction products predominate, the selectivity in the action of the catalyst increasing with increase in the contribution of the reaction initiating process in accordance with the end group route.

It has been suggested that the equation for the rate of degradation of polyalkenes with allowance for the stationary nature of the concentration of the active centres for the depolymerisation of macromolecules and the rapid chain propagation in depolymerisation be used to estimate the rate constants for both random initiation (k_{ic}) and initiation in accordance with the end group route (k_{it}), as well as the corresponding lengths of the kinetic chains (z_c and z_t).[8,9,42]

$$\frac{d[P]}{dt} = z_t k_{it} c + z_c k_{ic} [P], \quad (1)$$

where [P] is the concentration of the polymer and c the concentration of the terminal double bonds varying in accordance with the exponential law

$$c = c_0 \exp(-k_{it} t).$$

Here c_0 is the initial content of the double bonds.

The solution of Eqn (1) yields

$$[P] = \exp(-k_{it} z_t t) + \frac{k_{it} z_t c_0}{k_{it} - k_{ic} z_c} [\exp(-k_{it} t) - \exp(-k_{ic} z_c t)]. \quad (2)$$

The quantities k_{it}, k_{ic}, z_t, and z_c may be determined in the initial stages of the degradation process where $[P] \ll 1$ and $t \ll 1/k_{it}$. In this case, it is permissible to disregard the change in the concentration of the terminal double bonds. The decrease in the amount of the polymer (expressed as fractions of the initial amount) is then described by the equation

$$[P] = 1 - k_{ic} z_c t - k_{it} z_t c_0 t. \quad (3)$$

The kinetic parameters obtained for to the thermocatalytic degradation of polyisobutylene[9] in the presence of a catalyst with a moderate relative acidity (from 1.4 to 2.3 mequiv. per gramme of the catalyst) are presented in Table 4. Regardless of the chemical structure of the catalyst, the numerical values of both k_{it} and k_{ic} hardly change (within the limits of error). This confirms (taking into account the overall yield of the gaseous products and also the content of iso-C_4 hydrocarbons) the conclusion that the activity and the selectivity of electrophilic

Table 4. Principal kinetic parameters of the catalytic degradation of polyisobutylene.

Catalyst	T/K	$10^6 k_{ic}/s^{-1}$	$10^6 k_{it}/s^{-1}$	z_c	z_t
$H[Na(C_2H_5)AlCl_3OH]$	473	0.45	3.50	8	8
	493	0.48	2.50	7	16
	513	1.12	2.10	4	26
	533	1.50	1.90	3	37
$H[NaAlCl_4OH]$	473	0.53	3.50	7	4
	493	0.62	3.30	5	9
	513	0.80	2.90	5	15
	533	1.20	2.50	4	20
$H[Mg(C_2H_5)AlCl_4OH]$	473	0.36	4.90	12	10
	493	0.45	3.10	11	21
	513	0.69	2.40	9	33
	533	0.89	2.20	8	42
$2MgCl_2 \cdot AlCl_3 \cdot H_2O$	473	0.54	4.60	9	7
	493	0.77	2.70	7	17
	513	1.07	2.20	6	28
	533	1.17	2.00	6	39

Note. Reaction conditions: [Cat] = 1×10^{-3} mol (g PIB)$^{-1}$. The errors are $\pm 3\%$ in the determination of k and $\pm 5\%$ in the determination of z.

catalysts, in particular complexes based on metal chlorides, are related to their relative acidity index. The ratio of k_{it} and k_{ic} (Table 4) indicates the preferential initiation of the depolymerisation of the macromolecules in accordance with the end group route at relatively low temperatures of the degradation of the polymeric product. With increase in the process temperature, the contribution of random reactions increases, but the decrease under these conditions in the length of the kinetic chain in the decomposition of polyalkenes for random process initiation (z_c) compared with the length of the kinetic chain for initiation in accordance with the end group route (z_t) may be only apparent. The actual increase in the number of monomer units formed for the random initiation of the process also occurs, since the energy of the β-decomposition of the carbonium ion diminishes under these conditions, but, against the background of the sharp increase in the number of breaks in the macrochains, the degradation of the macromolecules is not manifested.

For low degrees of polymerisation ($\bar{P}_n^0$), the values of z_t are actually equal to the chain length in the depolymerisation of macromolecules. For high values of $\bar{P}_n^0$, z_t becomes constant, which is evidently determined by the relative contributions of the chain propagation and destruction reactions on the carbonium ion active centres formed from the end groups.[8,9]

The presence of a tertiary carbon atom and especially of the C=C double bonds (both terminal and internal) in the macromolecules exerts a signficant influence on the thermocatalytic degradation of polyalkenes. In particular, process initiation predominantly in accordance with the end group route is characteristic of low-molecular-mass PIB specimens with a high relative content of C=C double bonds (Fig. 1), because in the course of the thermocatalytic decomposition of the polymer a slight change in the molecular masses of the polymeric products is observed (in the initial stages of the process, $\bar{P}_n/\bar{P}_n^0 \approx 1$). The ratio $\bar{P}_n/\bar{P}_n^0$ diminishes only for high degrees of conversion. For high-molecular-mass PIB specimens, isobutene–isoprene copolymers containing labile bonds at the junctions between the isobutene clusters and the isoprenyl unit with a C=C bond, and polyethylene (PE) (regardless of its molecular mass) containing internal vinylidene and *trans*-vinylidene C=C bonds, the overall degradation of the macromolecules proceeds simultaneously both as a random process and

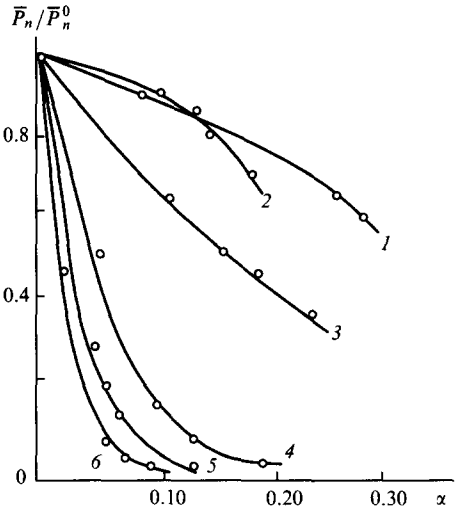


Figure 1. Dependence of the relative degree of polymerisation on the extent of reaction (α) during the thermal catalytic degradation of polyisobutylene (PIB) at 573 K in the presence of $H[NaAlCl_4OH]$. Catalyst concentration 1×10^{-3} mol (g PIB)$^{-1}$. Initial degree of polymerisation of PIB: (*1*) 17; (*2*) 20; (*3*) 49; (*4*) 360; (*5*) 1790; (*6*) 3570.

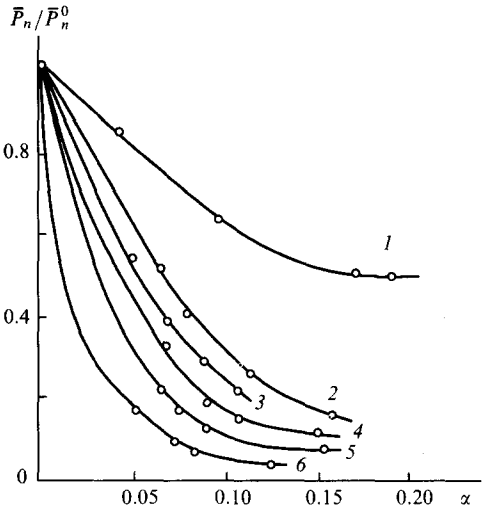


Figure 2. Dependence of the relative degree of polymerisation on the extent of reaction (α) of low pressure polyethylene (LPPE) during thermocatalytic degradation at 633 K in the presence of $H[NaAlCl_4OH]$. Catalyst concentration 1×10^{-3} mol (g LPPE)$^{-1}$. Initial degree of polymerisation of LPPE: (*1*) 2×10^4; (*2*) 6×10^4; (*3*) 1.45×10^5; (*4*) 2.5×10^5; (*5*) 2.7×10^5; (*6*) 8.7×10^5.

in accordance with the end group route, but with different contributions of these mechanisms to the overall process (Fig. 2). The possibility of the initiation of the degradation of macromolecules also via the vinyl end groups cannot be ruled out.

In the general case, the thermocatalytic degradation reactions of polyalkenes are initiated as follows:

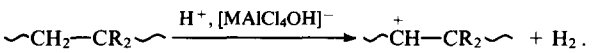
(a) the end group route:

(b) the random route:

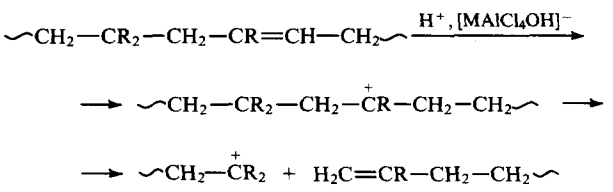
$$\sim CH{=}CR_2 \xrightarrow{H^+,[MAlCl_4OH]^-} \sim CH_2{-}\overset{+}{C}R_2,$$

R = CH_3 (PIB, BR), H (PE);

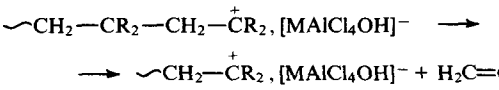
(b) the random route:



The random route in relation to BR and PE:

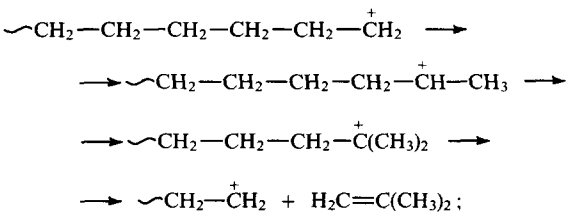


The modes of the chain propagation reactions in the course of the decomposition of macrocations may differ significantly depending on the structure of the selected polymer. For example, in the thermocatalytic degradation of PIB and BR, the carbonium ions formed decompose by β-elimination of the monomer—in the given instance isobutene (Table 3):

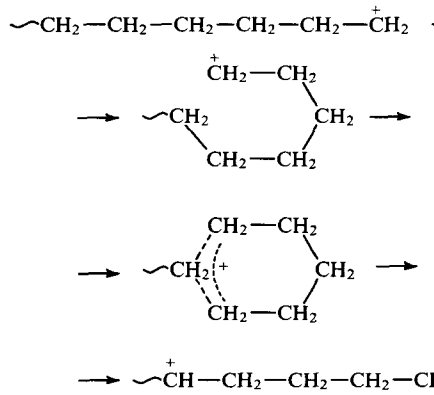


In the thermocatalytic degradation of PE, the linear carbonium ion $R-{}^{+}CH_2$ formed in the reaction can react via two main paths:

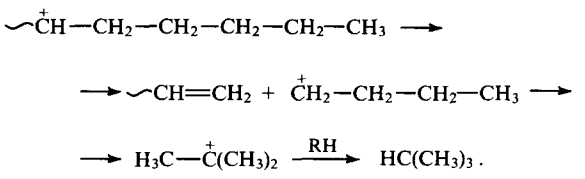
(1) as a result of skeletal isomerisation with formation of a tertiary carbonium ion, which decomposes further into a new carbonium ion and isobutene:



(2) as a result of the isomerisation of the macrocation accompanied by the transfer of the excess positive charge to the sixth carbon atom via an intermediate reaction involving the cyclisation of 'flexible' sequences made up of methylene groups:

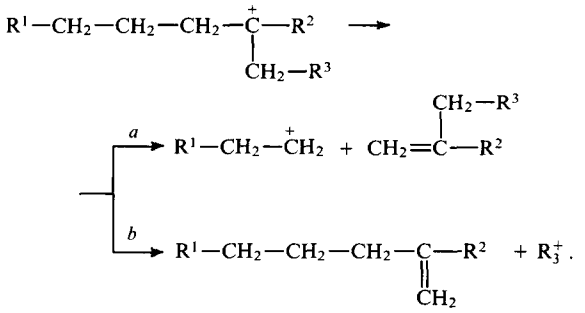


The β-decomposition of the carbonium ion formed and subsequent isomerisation reaction and the reaction involving the abstraction of a proton from the neutral polymer molecule lead to the formation of isobutane (Table 3):



We may note that this reaction does not correspond to the classical mechanism of the PE depolymerisation process, but can be regarded as a coupled reaction involving the degradation of macromolecules and chain transfer.

In the thermocatalytic decomposition of PE, the macromolecules of which contain branches, for example, high pressure polyethylene (HPPE), the carbonium ions may be formed not only from the C=C double bonds but also from a tertiary carbon atom. The subsequent degradation of the polymeric carbonium ions proceeds via two paths: degradation of the main chain (*a*) and decomposition of the polymeric carbonium ion with elimination of the surrounding group (chain branching) (*b*):



A new carbonium ion, undergoing further decomposition, as well as 'dead' polymer, the macromolecule of which contains a vinylidene bond, are formed in both cases.

Thus the presence of a tertiary carbon atom and especially of C=C double bonds in the polymer chains plays an important role in the initiation of the degradation of the macromolecules and in the propagation of the thermocatalytic electrophilic degradation of polyalkenes. The stability of polyalkenes in their thermocatalytic electrophilic degradation diminishes in the following sequence: high pressure polyethylene > low pressure polyethylene > polypropylene > poly-isobutylene > butyl rubber,[42] i.e. an increase in the degree of substitution of the carbon atoms in the macromolecules leads to a decrease in the stability of the latter.

IV. Hydrogenolysis (dehydrosulfurisation) of organosulfur compounds

The complexes of metal chlorides having an acidity lower than $AlCl_3$, in particular $H[MAlCl_4OH]$ (M = Li, Na, K) and other compounds of this type, formed as a result of the interaction of $AlCl_3$ with Group I and II metal chlorides (with H_2O as the cocatalyst),[55] exhibit a fairly high activity and selectivity in the reactions involving the hydrogenolysis of organosulfur compounds of different classes (mercaptans, sulfides, disulfides, thiophene) and accompanied by the elimination of H_2S.[56–61] The process proceeds under mild conditions (450–625 K, atmospheric pressure) and does not require the introduction of molecular hydrogen into the reaction zone (Tables 5 and 6).

The nature and structure of the molecules of the hydrocarbon solvent, which behaves as a hydrogen donor, exert an appreciable influence on the extent of the reaction. The most suitable solvents are naphthene hydrocarbons, which is due to their high proton-donating capacity compared with paraffins having the normal structure and especially arenes.

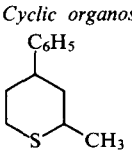
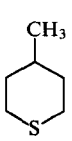
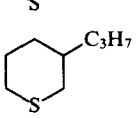
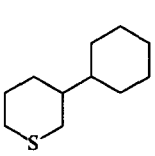
On the basis of experimental data for the hydrodesulfurisation of the naphthene fractions of hydrocarbons[57] and also

Table 5. Gaseous products of the hydrogenolysis of certain organosulfur compounds.

Catalyst	Content of gaseous products (vol.%)											Conversion with respect to S (mass %)	Catalyst selectivity (relative units)
	H_2	H_2S	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	iso-C_4H_{10}	n-C_4H_{10}	ΣC_4H_8	ΣC_5		
Hexanethiol													
H[LiAlCl$_4$OH]	2.2	15.3	9.91	16.65	17.52	9.30	1.91	11.30	11.32	4.59	—	46	0.7
H[NaAlCl$_4$OH]	2.5	16.84	11.46	11.95	4.99	1.86	11.4	18.0	6.00	11.0	4.0	47	0.9
H[KAlCl$_4$OH]	2.0	20.85	4.43	3.47	traces	6.62	23.78	22.32	11.16	2.53	2.84	23	0.8
Dihexyl sulfide													
H[NaAlCl$_4$OH]	1.38	13.31	6.12	3.90	1.84	6.33	13.0	26.23	19.16	8.39	—	33	0.7
Thiophene													
H[NaAlCl$_4$OH]	5.29	40.19	10.07	4.67	2.07	0.8	1.25	10.23	12.56	0.24	12.63	7	0.3

Note. Reaction conditions: $T = 523$ K, reaction time 30 min, [Cat] = 1 M, solvent — dodecane.

Table 6. Rate constants for the desulfurisation of certain organosulfur compounds.

Compound	Degree of conversion with respect to S (mass%)	$10^4 K/s^{-1}$	Selectivity (relative units)
Acyclic organosulfur compounds			
$C_6H_5CH_2SCH_2C_6H_5$	83	8.5	0.9
$C_6H_5SC_{10}H_{21}$	80	7.8	0.8
$C_6H_5SC_3H_7$	70	5.5	0.7
iso-$C_5H_{11}SC_3H_7$-n	50	3.3	0.6
tert-$C_6H_{13}SC_6H_{13}$-n	40	2.3	0.5
n-$C_6H_{13}SC_6H_{13}$-n	33	1.8	0.5
n-$C_6H_{13}SH$	47	220	0.9
n-$C_6H_{13}SH$ [a]	51	170	0.7
n-$C_6H_{13}SH$ [b]	37	230	0.8
Cyclic organosulfur compounds			
	90	6.7	0.9
	60	4.5	0.6
	45	3.3	0.5
	40	2.5	0.5
	35	2.0	0.4
	25	0.3	0.3

Note. Reaction conditions: T = 523 K, catalyst — H[NaAlCl$_4$OH], [Cat] = 1 M, solvent — dodecane.
[a] Catalyst — H[LiAlCl$_4$OH]; [b] catalyst — H[KAlCl$_4$OH].

certain individual organosulfur compounds in hydrocarbon solvents,[58] the catalytic systems H[MAlCl$_4$OH] can be arranged in the following sequence in terms of their activity and the selectivity of their action: H[LiAlCl$_4$OH] > H[NaAlCl$_4$OH] > H[KAlCl$_4$OH]. This sequence agrees with the variation of their acid strength (pK_a, q_{H^+}, RAI) (Table 1).

In all cases, the desulfurisation of organosulfur compounds is accompanied by the formation of gaseous and liquid products (Tables 5 and 7), the main gaseous reaction product at 450–475 K being H_2S (96–98 mass%) under these conditions.

The heterophase, i.e. in the presence of H[MAlCl$_4$OH], hydrogenolysis of organosulfur compounds is complex in view of the occurrence of a series of consecutive-parallel chemical reactions with participation of the hydrocarbon solvent as a proton donor — as a consequence of the polyfunctionality of the action of the catalyst. The process is described by the kinetic equations for topochemical reactions of the Avrami–Erofeev type:[62]

$$c(\tau) = c(\tau_0)\exp[-k(\tau)^n],$$

where $c(\tau_0)$ and $c(\tau)$ are the initial and current concentrations of the reactants respectively, k is the observed rate constant for the reaction of the organosulfur compounds, and n is the reaction order. At the same time, the rate constants for the hydrogenolysis of the organosulfur compounds were estimated from the initial sections of the kinetic curves for low degrees of conversion assuming that the process obeys first-order reaction conditions. The molecular structure of the organic sulfur-containing compounds exerts an appreciable influence on the rate of hydrogenolysis and they can be arranged in the following sequence in terms of their reactivities: hexanethiol > dihexyl sulfide > thiophene. This follows with the strength of the C–S bond in these molecules.[63]

In the desulfurisation of sulfides (Table 6), the reactivity of the compounds investigated varies in the following sequence:
(a) acyclic sulfides:

$$C_6H_5(CH_2)_2-S-(CH_2)_2C_6H_5 > C_6H_5-S-C_{10}H_{21} > \text{iso-}C_5H_{11}-S-C_3H_7\text{-n} > C_6H_5-S-C_3H_7 > \textit{tert}\text{-}C_6H_{13}-S-C_6H_{13}\text{-n} > \text{n-}C_6H_{13}-S-C_6H_{13}\text{-n};$$

(b) cyclic sulfides:

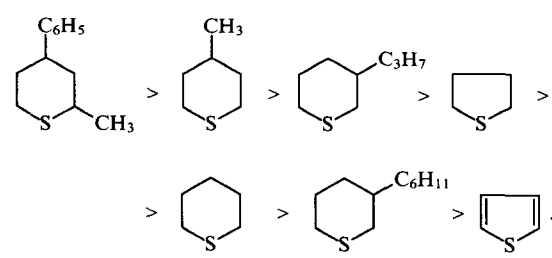
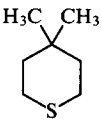
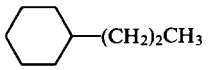
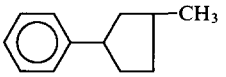
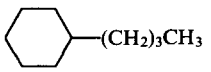
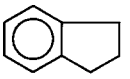
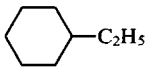
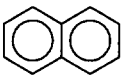
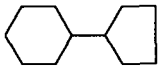
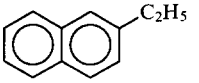
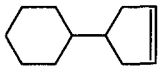
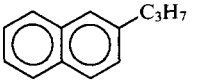
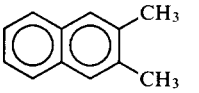
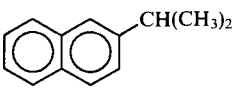
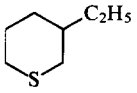
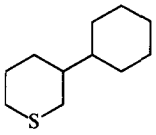


Table 7. Liquid products of the reactions of certain cyclic sulfides (Schemes 1 and 2).

Products of reaction of 3-cyclohexylthiacyclohexane	Content (mass %) at t = 15 min	Content (mass %) at t = 60 min	Products of reaction of 2-methyl-4-phenylthiacyclohexane	Content (mass %) at t = 15 min	Content (mass %) at t = 60 min
$n\text{-}C_9H_{20}$	3.5	1.0	$n\text{-}C_{12}H_{26}$	30.9	26.9
$n\text{-}C_{10}H_{22}$	10.2	2.7	$iso\text{-}C_{12}H_{26}$	34.0	36.8
$n\text{-}C_{11}H_{24}$	10.8	0.8		7.1	—
$n\text{-}C_{12}H_{26}$	29.9	32.6	$C_6H_5C_2H_5$	—	3.4
$iso\text{-}C_{12}H_{26}$	12.5	22.3	$C_6H_5CH(CH_3)_2$	2.2	3.9
$C_2H_5CH(CH_3)(CH_2)_3CH_3$	2.8	4.7	$C_6H_5CH=CH_2$	5.0	1.9
	11.3	11.9		4.9	5.2
	2.5	1.7		6.9	4.7
	1.5	2.0		1.6	—
	8.7	16.2		3.8	6.5
	—	2.8		1.3	2.4
	1.8	—		2.9	4.6
	1.3	—		—	3.7
	0.9	—			
	2.3	1.3			

Note. Reaction conditions: T = 523 K, catalyst — $H[NaAlCl_4OH]$, [Cat] = 1 M, solvent — dodecane (t = reaction time).

Evidently, enhancement of the electron-donating properties of the substituent (taking into account its position relative to the S atom in the cyclic sulfides) weakens the C–S bond. The reactivity of cyclic sulfides diminishes in the presence of bulky substituents capable of giving rise to steric hindrance in the hydrogenolysis of organic thiacycloalkanes. The desulfurisation of organic sulfides is favoured by an increase in the degree of branching in the hydrocarbon fragment, which is also due to the enhancement of the electron-donating functions of the substituent.

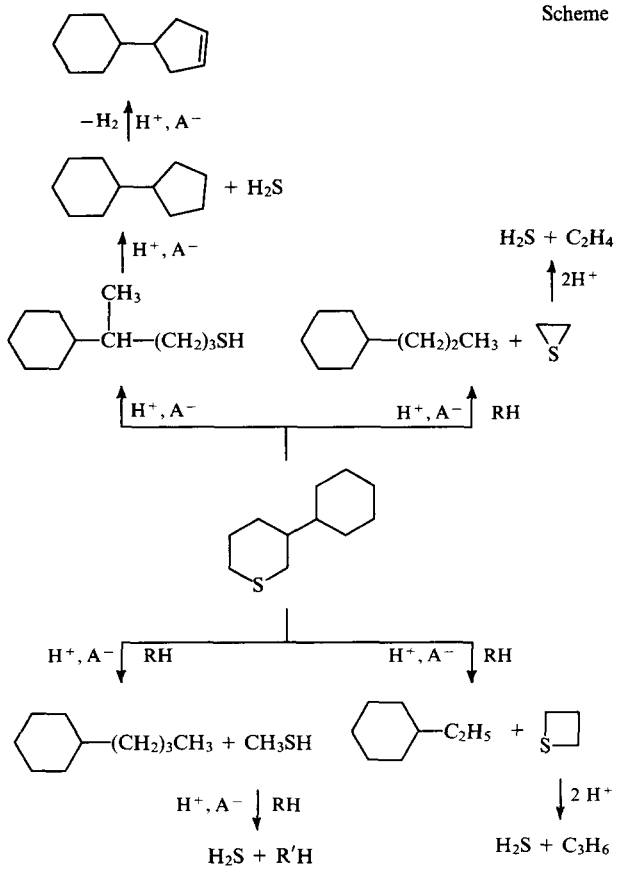
The molecular structure of organic sulfur-containing compounds (both isotypical and belonging to different classes) does not affect the mode and course of the hydrogenolysis. This is seen, in particular, from the comparison of the compositions of the liquid products formed in the desulfurisation of 3-cyclohexylthiacyclohexane and 2-methyl-4-phenylthiacyclohexane in the presence of $H[NaAlCl_4OH]$ (Table 7). The dissociation of the C–S bond in the thiacyclohexane ring and its further reactions, as well as the dissociation of the C–C bond between the thiacyclohexane ring and the surrounding groups with their subsequent reactions are characteristic of the desulfurisation process. The process proceeds as a series of parallel-consecutive electrophilic reactions.

The principal types of the hydrogenolysis of 3-cyclohexylthiacyclohexane in the presence of $H[NaAlCl_4OH]$ (or H^+A^-) in dodecane are presented in Scheme 1.

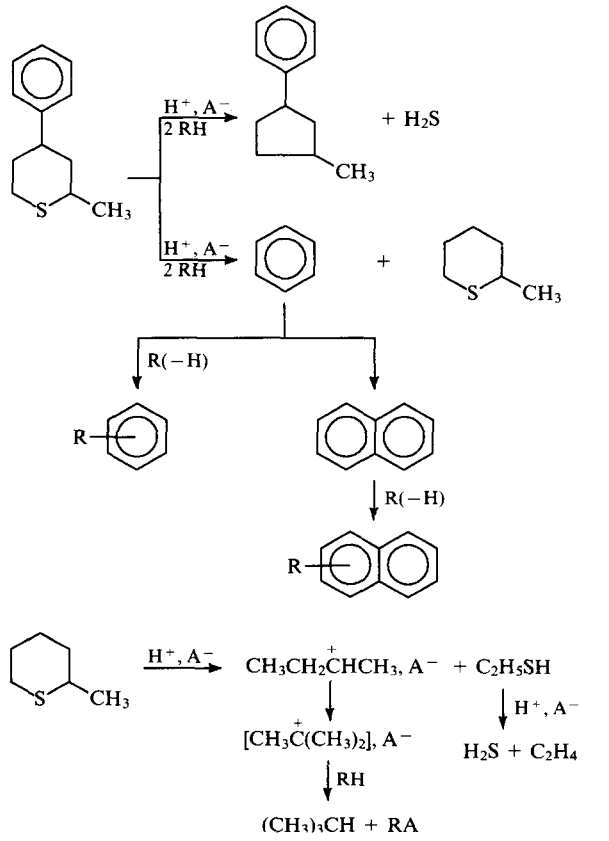
The virtual absence of sulfur-containing compounds 0.5–1 h after the start of the reaction (at 523 K) and the complete absence of mercaptans from the reaction products even in the early stages of the hydrogenolysis of cyclic sulfides (5–10 min) are striking. Furthermore, in the purely thermal decomposition and also in the presence of oxide catalysts, for example alumina–cobalt oxide–molybdenum oxide catalysts, the thiacyclanes react via a stage involving the formation of mercaptans.[64]

The possible types of the hydrogenolysis of 2-methyl-4-phenylthiacyclohexane under the same conditions are illustrated in Scheme 2.

Scheme 1

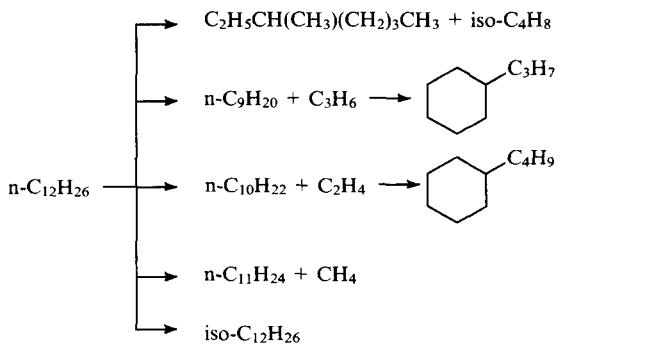


Scheme 2

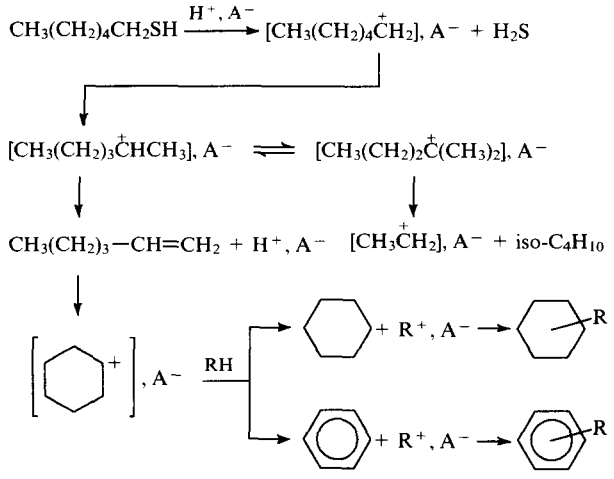


On the basis of these experimental data and also the fact that the rate of hydrogenolysis of mercaptans is 1–2 orders of magnitude higher than that of thiacyclanes (Table 6), one may postulate that mercaptans as well as thiirane, thiacyclopropane, 2-ethylthiacyclohexane, and dimethylthiacyclohexane (Table 7) participate in the process as intermediates. This is reflected in Schemes 1 and 2. Saturated aliphatic C_8-C_{11} hydrocarbons and iso-$C_{12}H_{26}$ are formed as a result of the reactions of the solvent (dodecane). Some of the alkanes are transformed into naphthene derivatives (Scheme 3).

Scheme 3



Thus, in the presence of complexes of metal chlorides with proton-donating compounds, the desulfurisation of cyclic sulfides proceeds via a single mechanism: the hydrogenolysis of the C–S bond with formation of H_2S and the heterolytic dissociation of the C–C bonds between the thiacyclane ring and the surrounding groups and also directly in the ring. The process takes place with participation of ions. The C–S bond and subsequently the C–C bonds of the hydrocarbon fragment dissociate also in the hydrogenolysis of mercaptans.



Thus electrophilic catalysts based on $H[MAlCl_4OH]$ exhibit a fairly high activity and selectivity in the catalytic hydrogenolysis reactions of various sulfur-containing organic compounds proceeding via the carbonium ion mechanism at relatively low temperatures (470 ± 50 K). An important factor is that the reaction proceeds at the normal pressure and does not require the additional introduction of molecular hydrogen; the higher the acidity of the electrophilic catalyst, the more active but less selective the catalytic system under these conditions.

V. Dehydrogenation and hydrogenation of hydrocarbons

The complexes of metal chlorides with proton-donating compounds are capable of initiating both dehydrogenation[65] and hydrogenation reactions of hydrocarbons. The study of the hydrogenolysis reactions of sulfur-containing compounds (Table 5) and degradation reactions of hydrocarbons (Table 8) in the presence of Brønsted acids based on $AlCl_3$ and Group I and II metal chlorides showed that the mixture of gaseous reaction products contains as a rule molecular hydrogen. In particular, the thermocatalytic degradation of butyl rubber in the presence of $H[MAlCl_4OH]$ (M = Li, Na, K) is accompanied by the evolution of H_2 (up to 0.7 mass %). At the same time, in many instances anomalously high amounts of isobutane and other saturated hydrocarbons have been detected in the gaseous products (Tables 3, 5, and 8). The foregoing indicates the activity of catalysts of this type in both dehydrogenation and hydrogenation reactions of hydrocarbons under comparatively mild conditions (423 ± 40 K, atmospheric pressure).

The thermocatalytic dehydrogenation of hydrocarbons in the presence of $H[MAlCl_4OH]$ has been studied in fair detail in relation to low-molecular-mass model compounds — dodecane, decene, and cyclohexane (Table 8).[65] It is striking that the yield of molecular hydrogen in the dehydrogenation reactions of saturated and alicyclic hydrocarbons is always higher than in the dehydrogenation of alkenes. A similar conclusion can be reached also as regards saturated $C_3 - C_4$ hydrocarbons (propane, isobutane) (Table 8), which evidently indicates a large contribution of the coupled reaction involving the hydrogenation of unsaturated hydrocarbons formed in situ on decomposition of the initial alkanes in the presence of $H[MAlCl_4OH]$.

Typical H_2 elimination curves for the model dehydrogenation reaction of dodecane in the presence of $H[NaAlCl_4OH]$ are presented in Fig. 3*a*. The extrema on the curves indicate the simultaneous dehydrogenation of dodecane and the hydrogenation of the unsaturated hydrocarbon products catalysed by electrophilic catalysts with reduced acidity compared with $AlCl_3$, i.e. $H[NaAlCl_4OH]$, etc. The curves characterising the variation of the content of unsaturated hydrocarbons in the liquid products formed on decomposition of dodecane in the presence of $H[NaAlCl_4OH]$ (Figs. 3*a* and 3*b*) have a similar shape.

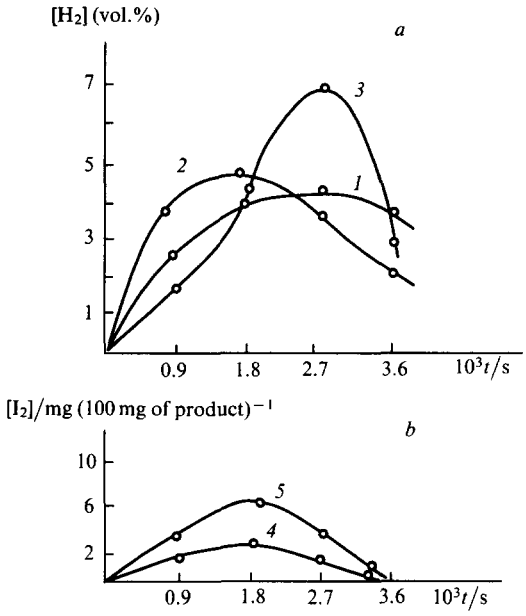


Figure 3. The hydrogen content in the gaseous products (*a*) and variation of the iodine number in the liquid products (*b*) during the catalytic conversion of dodecane in the presence of $H[NaAlCl_4OH]$ as a function of time at different process temperatures (T/K): (*1*) and (*4*) 473; (*2*) 500; (*3*) and (*5*) 525.

The compositions of the liquid products of the thermocatalytic degradation of dodecane, decene, and cyclohexane are presented in Table 9.

Experimental data show that two paths for the formation of molecular hydrogen in the thermal decomposition of hydrocarbons in the presence of $H[MAlCl_4OH]$ are possible: (1) degradation of the hydrocarbon molecules (decomposition via the C – C bonds); (2) cyclisation of unsaturated hydrocarbons with subsequent dehydrogenation of the resulting cyclic compounds. In both cases, the reactions proceed via the carbonium ion mechanism (Scheme 4):

Table 8. Gaseous products of the thermocatalytic decomposition of individual hydrocarbons in the presence of $H[NaAlCl_4OH]$.

Hydrocarbon	Content of gaseous products (vol.%)								
	H_2	CH_4	ΣC_2	C_3H_6	C_3H_8	iso-C_4H_8	iso-C_4H_{10}	ΣC_4	C_5 and above
Dodecane	9.74	1.3	3.30	0.51	10.14	21.35	41.92	74.46	0.55
Dec-1-ene	1.72	0.80	3.52	2.50	1.62	50.22	33.86	88.61	1.23
Cyclohexane	8.25	—	traces	0.22	6.18	15.40	49.54	67.72	17.63

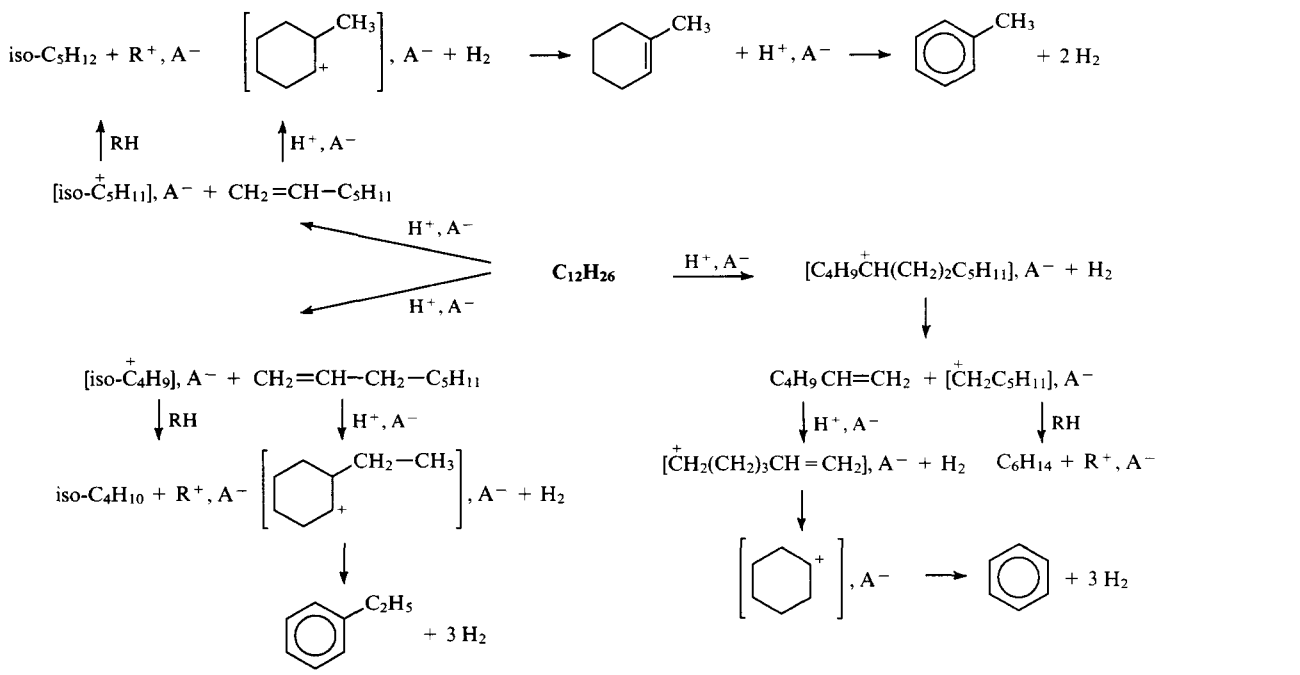
Note. Reaction conditions: T = 523 K, reaction time 30 min, catalyst : hydrocarbon = 1 : 4.

Table 9. Liquid products of the thermocatalytic decomposition of individual hydrocarbons in the presence of $H[NaAlCl_4OH]$.

Hydrocarbon	Content of liquid products (mass %)									
	C_6H_{14}	C_6H_{12}	cyclo-C_6H_{12}	C_6H_6	$C_6H_5C_2H_5$	$C_6H_5CH_3$	$C_6H_4(CH_3)_2$	other products	iso-$C_{10}H_{22}$	iso-$C_{12}H_{26}$
Dodecane	5.0	—	2.3	2.4	0.8	7.9	15.0	36.3	—	30.3
Dec-1-ene	9.5	8.5	7.1	5.5	—	4.1	—	—	65.3	—
Cyclohexane	2.6	—	—	76.3	—	—	21.1	—	—	—

Note. The reaction conditions are indicated in Table 8.

Scheme 4



The formation of anomalously large amounts of unsaturated hydrocarbons in the thermooxidative decomposition of polyalkenes and also of individual saturated and unsaturated compounds in the presence of catalysts — Brønsted acids based on complexes of $AlCl_3$ and Group I and II metal chlorides (Tables 3, 5, 8, and 9) — can be explained by the fact that electrophilic chemical reactions of two types can occur under the given conditions: (1) the interaction of alkenes with alkanes (alkylation); (2) dehydrogenation of the resulting unsaturated hydrocarbons in the presence of H[MAlCl$_4$OH]:

$$CH_2{=}C(CH_3)_2 \xrightarrow{H^+, A^-} (CH_3)_3\overset{+}{C}, A^-$$

$$(CH_3)_3\overset{+}{C}, A^- + \sim CH_2{-}C(CH_3)_2H \longrightarrow$$

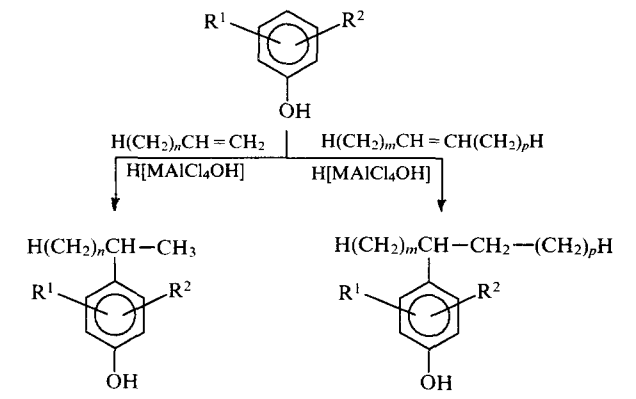
$$\longrightarrow (CH_3)_3CH + \sim CH_2{-}\overset{+}{C}(CH_3)_2, A^-, \text{ etc.}$$

Thus electrophilic catalysts with an acidity reduced compared with $AlCl_3$ are capable of initiating the dehydrogenation and hydrogenation reactions of hydrocarbons proceeding via the carbonium ion mechanism. The active forms of the catalyst are the corresponding Brønsted acids.

VI. Alkylation of phenols by polyalkenes

The Friedel–Crafts alkylation of phenols by alkenes (Scheme 5) belongs to the group of fairly complex reactions involving electrophilic substitution in aromatic hydrocarbons. As a rule the substitution is accompanied by the formation of very appreciable amounts of secondary products, especially when electrophilic reaction catalysts with high relative acidity indices, in particular $AlCl_3$, BF_3, $SnCl_4$, $ZnCl_2$, H_2SO_4, etc., are employed (Table 10). For example, in the reactions of higher α-alkenes with phenols in the presence of $AlCl_3$, the products of the decomposition the phenols (butylphenols, etc.)[66] as well as the products of the interactions of the phenols with $AlCl_3$ (the corresponding salts of HCl)[67] are formed together with alkylphenols.

Scheme 5



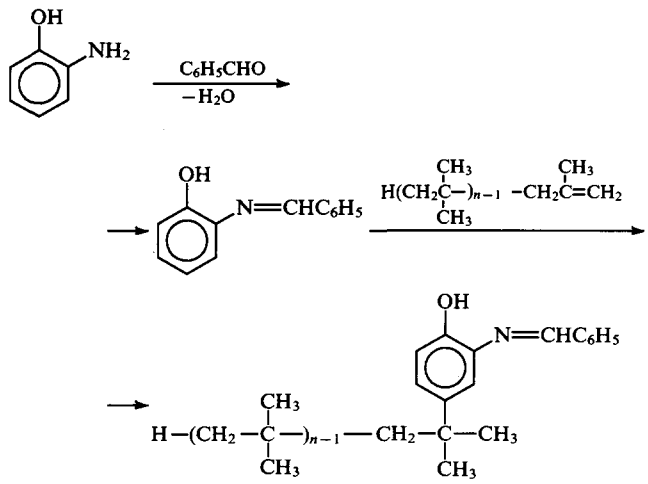
$m + p = n - 1$;
$R^1 = R^2 = H$;
$R^1 = H$, $R^2 = o$-, m-CH_3; $R^1 = H$, R^2 = iso-C_3H_7;
$R^1 = R^2 = tert$-C_4H_9; $R^1 = H$, $R^2 = o$-, m-, p-OH.

The ease of the alkylation of phenols by polyalkenes increases after the introduction of electron-donating substituents (HO, H_2N) into monohydric phenols, but diminishes in the presence of two and more bulky substituents in the aromatic ring, which give rise to steric hindrance.

The kinetics of the alkylation of phenols by alkenes have been investigated in relation to the model reaction of phenol with hept-1-ene — $T = 343$ K, identical concentrations of phenol and the alkene (2.4 M), and H[NaAlCl$_4$OH] concentration 0.24 M. The process follows second-order kinetics and the observed rate constant is $(2.2 \pm 0.2) \times 10^{-5}$ litre mol^{-1} s^{-1}.

The interaction of aminophenols with polyalkenes in the presence of H[MAlCl$_4$OH] and other similar Brønsted acids with a reduced acidity compared with $AlCl_3$ involves the amino-groups and not the aromatic ring. Nevertheless, the possibility of the ring-alkylation of aminophenol derivatives (in particular Schiff bases) by polymers under these conditions has been demonstrated (Scheme 6).

Scheme 6



The alkylation of phenols by unsaturated polymeric hydrocarbons proceeds in an even more complex manner because there is a sharp increase in the number of probable secondary reactions such as isomerisation, depolymerisation, and degradation of the polymeric fragments in the initial (polyalkenes) and final (polyalkenylphenols) products. This had been demonstrated earlier in relation to the interaction of polyalkenes with phenol in the presence of benzenesulfonic acid (Table 10).[68]

Systems of the type H[MAlCl$_4$OH], with a reduced relative acidity (Table 1), proved to be more convenient and effective catalysts of the selective alkylation of phenols by polyalkenes than AlCl$_3$. They exhibit a high activity and selectivity in the reactions of phenols with polyalkenes[69,70] occurring under mild conditions (378 ± 15 K, reaction time 3 ± 1 h), which lead to polyalkenylphenols in nearly quantitative yields (90 mass% and above) (Table 10).

Thus the decrease in the acidity of the metal chloride-based catalytic systems (evidently up to a certain limit) lowers (as in the cases examined above) the contributions of the secondary and

Table 10. Polymer-analogue reactions of polyalkenes in the presence of H[MAlCl$_4$OH].

Phenol	Catalyst	Reaction time/h	Yield of product (mass%)	[C=C]/(mol PIB)$^{-1}$	^{13}C NMR spectrum,[a] δ/ppm	Selectivity (relative units)
Polyethylene ($\overline{M}_n$ = 1300)						
Phenol	H[AlCl$_3$OH]	10	75	—	—	0.7
Phenol	C$_6$H$_5$SO$_3$H	4	46	—	—	0.4
Phenol	H[NaAlCl$_4$OH]	2.5	96	0.012	135.5	0.9
2-Methylphenol	H[NaAlCl$_4$OH]	2.5	96	0.015	135.2	0.9
3-Methylphenol	H[NaAlCl$_4$OH]	3.0	93	0.021	134.8	0.9
4-Isopropylphenol[b]	H[NaAlCl$_4$OH]	3.0	93	0.021	129.6	0.9
2,6-Di-*tert*-butylphenol[b]	H[NaAlCl$_4$OH]	4.0	89	0.033	135.2	0.9
o-Dihydroxybenzene	H[NaAlCl$_4$OH]	2.5	93	0.021	149.0	0.9
m-Dihydroxybenzene	H[NaAlCl$_4$OH]	2.5	96	0.012	122.8	0.9
p-Dihydroxybenzene	H[NaAlCl$_4$OH]	2.5	90	0.030	131.6	0.9
2-Aminophenol[c]	H[NaAlCl$_4$OH]	2.5	93	0.021	—	0.9
4-Aminophenol[c]	H[NaAlCl$_4$OH]	2.5	98	0.006	—	0.9
2-Benzylideneaminophenol[d]	H[NaAlCl$_4$OH]	4.0	98	0.012	136.9	0.9
4-Benzylideneaminophenol[d]	H[NaAlCl$_4$OH]	4.0	96	0.012	131.5	0.9
4-Isopropylphenol	H[LiAlCl$_4$OH]	2.5	91	0.023	—	0.9
m-Dihydroxybenzene	H[LiAlCl$_4$OH]	2.0	95	0.015	—	0.9
4-Isopropylphenol[b]	H[KAlCl$_4$OH]	2.5	93	0.021	—	0.9
m-Dihydroxybenzene	H[KAlCl$_4$OH]	2.0	96	0.012	—	0.9
Polypropylene ($\overline{M}_n$ = 1400)						
Phenol	C$_6$H$_5$SO$_3$H	4.0	36	—	—	0.3
Phenol	H[NaAlCl$_4$OH]	2.5	96	0.037	141.3	0.9
4-Isopropylphenol[b]	H[NaAlCl$_4$OH]	3.0	94	0.056	135.3	0.9
m-Dihydroxybenzene	H[NaAlCl$_4$OH]	2.5	98	0.019	128.5	1.0
4-Isopropylphenol[b]	H[LiAlCl$_4$OH]	3.5	92	0.074	—	0.9
m-Dihydroxybenzene	H[LiAlCl$_4$OH]	2.5	95	0.047	—	0.9
4-Isopropylphenol[b]	H[KAlCl$_4$OH]	3.0	94	0.056	—	0.9
m-Dihydroxybenzene	H[KAlCl$_4$OH]	2.5	97	0.030	—	0.9
Polyisobutylene ($\overline{M}_n$ = 1100)						
Phenol	C$_6$H$_5$SO$_3$H	4	31	—	—	0.3
Phenol	H[NaAlCl$_4$OH]	2.5	98	0.020	143.5	1.0
4-Isopropylphenol[b]	H[NaAlCl$_4$OH]	3.0	96	0.040	137.5	0.9
m-Dihydroxybenzene	H[NaAlCl$_4$OH]	2.5	98	0.020	130.7	1.0
4-Isopropylphenol[b]	H[LiAlCl$_4$OH]	3.0	95	0.050	—	0.9
m-Dihydroxybenzene	H[LiAlCl$_4$OH]	2.0	96	0.048	—	0.9
4-Isopropylphenol[b]	H[KAlCl$_4$OH]	3.0	96	0.040	—	0.9
m-Dihydroxybenzene	H[KAlCl$_4$OH]	2.0	94	0.060	—	0.9

Note. Reaction conditions: T = 383 K, [Cat] = 0.05 mol(mol polyalkene)$^{-1}$.
[a] Signal due to the carbon atom bound to the oligomeric radical; [b] T = 393 K; [c] T = 373 K; [d] [Cat] = 0.10 mol(mol polyalkene)$^{-1}$, T = 393 K.

side reactions, characteristic, for example, of catalytic processes involving the use of $AlCl_3$ or benzenesulfonic acid.[66,67] As a consequence of this, the selectivity of the action of these catalytic systems in these processes also increases.

Depending on the positions of the C=C bonds in the molecule of the initial polyalkene (terminal or internal), the corresponding polyalkenylphenols are formed; the reaction then proceeds via the classical electrophilic addition mechanism and the catalyst is a Brønsted acid: H^+, $[MAlCl_4OH]^-$.

Further reactions involving polyalkenylphenols and their derivatives may be carried out. In particular, polymeric ethers of (4-methyl-5,6-dihydro-2*H*-pyranyl)phenols have been obtained in this way.[69,71] In addition, polyalkenylphenols are of interest as stabiliser-antioxidants and also as additives to oils.

The presence of the benzylideneamino-group in the phenol ring hinders the electrophilic addition of polyalkenes to aminophenols owing to the depletion of the electron density of the aromatic ring. Benzylideneaminophenols therefore interact with polyalkenes under more several conditions than aminophenols or dihydric phenols.

VII. Dependence of the effectiveness of electrophilic catalysts on their acid–base properties

Experimental results obtained for a fairly large number of electrophilic reactions occurring in the presence of Brønsted acids indicate that the degree of conversion and the yield of the target products may vary within extremely wide limits in specific reactions depending on the nature and structure of the metal chlorides, the nature of the cocatalyst, the position of the corresponding metal in the Periodic System, and in essence (and evidently primarily) the acidity of the catalytic system. In particular, a relation has been traced between the acid–base properties of metal chloride complexes (taking into account the electronic configuration of the metal atom and also its position in the Periodic System) and their effectiveness and the selectivity of their action as catalysts for electrophilic processes. This can be seen in relation to the polymerisation reactions of isobutene from the C_4 hydrocarbon fractions[7,21,24] (Table 2), the degradation of hydrocarbons[3–5,36–49] (Table 3), the alkylation of phenols by polyalkenes[69,70] (Table 10), hydrogenolysis,[56–61] etc. Fig. 4 demonstrates to a first approximation the conventional boundary between the acid (electrophilicity and basic (nucleophilicity) properties of individual metal chlorides (straight line *AB*).

The metal chlorides located above the *AB* line or directly on it ($MgCl_2$, $BaCl_2$, $CaCl_2$, $SrCl_2$, $MnCl_2$, $CoCl_2$, $ZnCl_2$, $InCl_3$, $BiCl_3$, $SnCl_2$, $FeCl_2$) are characterised by a lower acidity than $AlCl_3$, $TiCl_4$, $SnCl_4$, and $FeCl_3$ and hence by a relatively mild catalytic activity. This is responsible for their fairly high activity and selectivity as catalysts of electrophilic processes. The metal chlorides located underneath the *AB* line, including $AlCl_3$, $SnCl_4$, $FeCl_3$, $TiCl_4$, etc., are 'hard' (strong) or 'superstrong' Lewis acids. Therefore their employment as catalysts for certain electrophilic reactions (for example, selective alkene polymerisation processes, degradation of polyalkenes and polydienes, desulfurisation of organosulfur compounds, alkylation of phenols and aminophenols by alkenes, polyalkenes, and polydienes, etc.) is not always effective, since undesirable side reactions may occur.

The results of theoretical calculations of the charges on the hydrogen atoms of the proton donors q_{H^+} in metal chloride-based complexes and other electrophilic compounds of the type of Brønsted acids[16] and also of the universal acidity index pK_a[14,15] in combination with experimental data on the relation between the acidity parameters of chemical compounds and the activity and selectivity of electrophilic catalysts in relation to the cationic polymerisation of alkenes[6–11] have led to a similar conclusion. An alternative measure of the acid strength of electrophilic catalysts is the relative acidity index [RAI/mequiv. (g. cat.)$^{-1}$, see

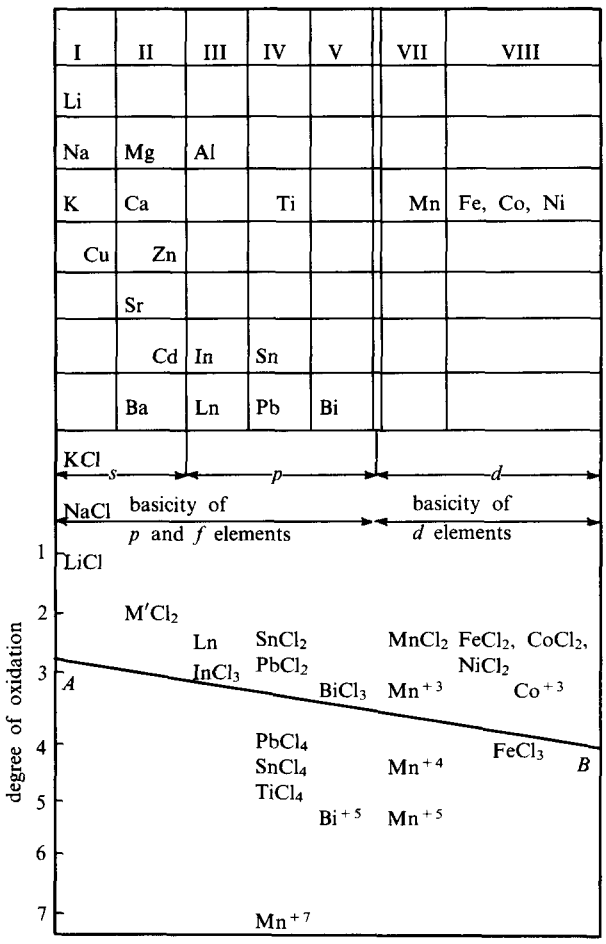


Figure 4. Variation of the acid–base properties of MCl_n as a function of the position of the metal in the Periodic System. M′ = Ba, Sr, Ca, Cd, Mg, or Zn.

Table 1],[13] which can be readily determined experimentally by differential nonaqueous titration [acetophenone (solvent)] and which does not require cumbersome theoretical calculations.

The data presented in Table 1 and also theoretical calculations,[6–11,14,15,21] have led to the discovery of a clear linear relation between the calculated (q_{H^+}, pK_a) and experimentally estimated (RAI) parameters of the acidity of the metal chloride-based complexes (in the form of Brønsted acids) (Fig. 5):

$$pK_a = 27.3 - 109.2\ q_{H^+},$$

(with a correlation coefficient of 0.98 and a standard error of 0.19);

$$RAI = 2.3 - 0.122\ pK_a,$$

and

$$RAI = 13.33\ q_{H^+} - 1.03,$$

(with a correlation coefficient of 0.99 and standard error of 0.085). The correlations between q_{H^+}, pK_a, and RAI are valid for an extremely large number of electrophilic catalytic systems based on metal chlorides and alkyl(aryl)metal chlorides involving Group IIA–VA and IIB–VIIIB metals, as well as relatively new catalytic systems based on metal chlorides and alkyl(aryl)metal chlorides involving Group IIIA metals with Group IA and IIA,B metal chlorides. Similar correlations have been observed for the complexes of boron fluorides and alkyl(aryl)boron fluorides with proton-donating compounds (H_2O, HF, ROH),[6–11] which in all probability makes it possible to reach a conclusion concerning the general

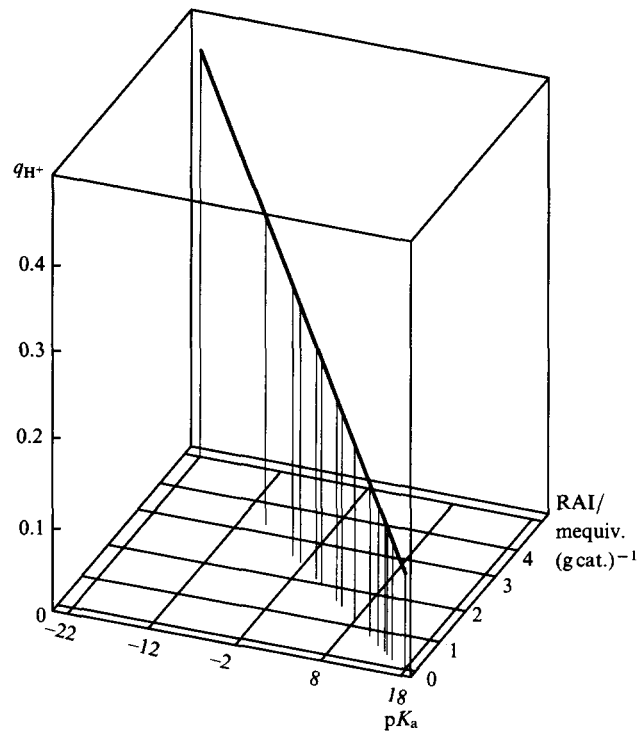


Figure 5. Relation between the parameters characterising the acidity of electrophilic catalysts (pK_a, RAI, q_{H^+}) (according to the data in Table 1).

character of both the methods for the estimation of the parameters of the acid strength of electrophilic chemical compounds and of the rather simple relation between them.

Analysis of the literature data and the results obtained[1-13, 17, 21, 25, 37, 40-49, 56-61, 69, 70] (Tables 1-4, 9, and 10) shows that the numerical values of the parameters characterising the acidity of electrophilic catalysts based on metal chloride complexes (q_{H^+}, pK_a, RAI) are a measure of their effectiveness and activity and of the selectivity of their action in various types of reactions occurring with participation of carbonium ions. The following rule is fairly strictly obeyed: the higher the relative acidity of the electrophilic systems formed in the interaction of Lewis acids with proton donors, the higher the activity but the lower the selectivity of the catalyst for processes occurring with participation of carbonium ions. Under these conditions (Fig. 6), there exist both an upper limit (the catalyst is extremely active, the contribution of side and secondary reactions is large) and a lower limit (extremely low activity of the catalyst) to the effectiveness of the action of catalytic systems (Fig. 6):

(a) $pK_a \gg 11$ [RAI $\leqslant$ 0.9 mequiv. (g cat.)$^{-1}$]—low acidity parameters; such catalytic systems are inactive in many electrophilic processes or their activity is low {ROH, H_2O, $H[R_3AlOH]$, $H[R_3AlOR]$, etc.};

(b) $-10 \ll pK_a \ll +11$ [RAI in the range from 0.9 to 3.0 mequiv. (g. cat.)$^{-1}$]—optimum acidity parameters: the catalytic systems exhibit a fairly high activity and selectivity:

(c) $pK_a \leqslant -10$ [RAI $\geqslant$ 3.0 mequiv. (g cat.)$^{-1}$]—high acidity parameters. In this case an extremely high activity but as a rule a low selectivity are characteristic of the catalytic systems {$H[AlCl_3OH]$, $H[BF_4]$, etc.}.

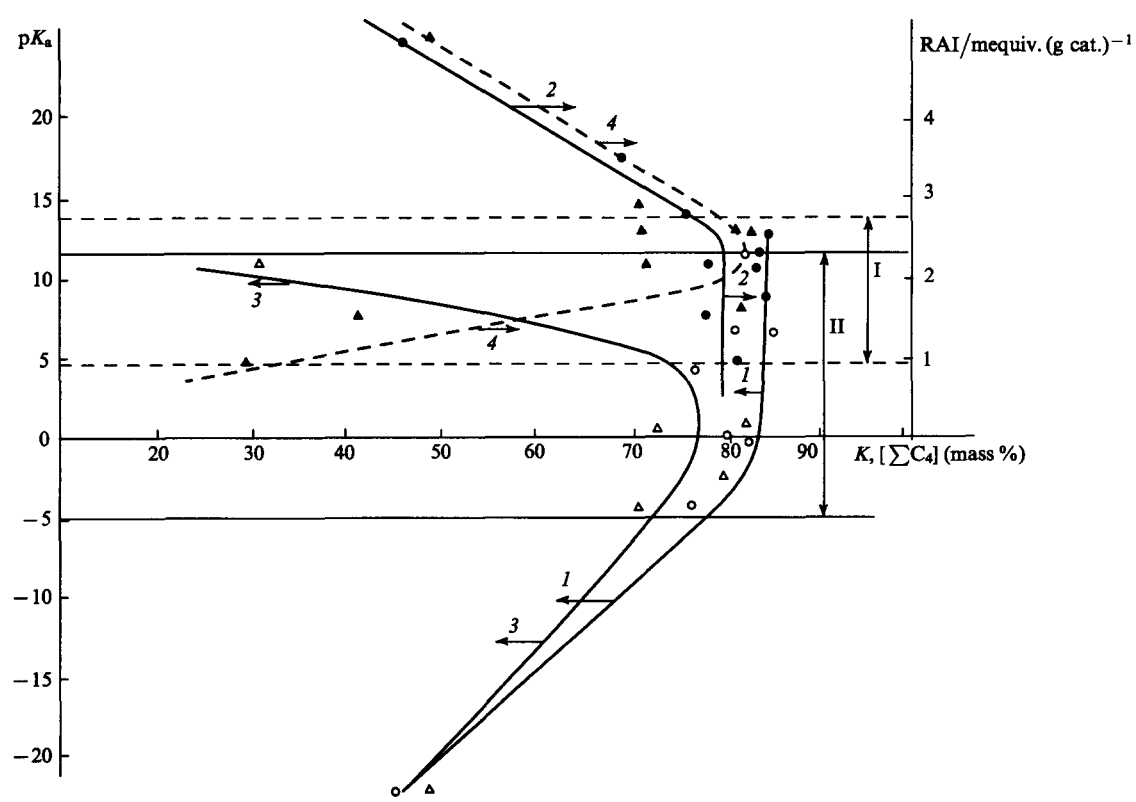


Figure 6. Conventional regions of the optimum values of pK_a (continuous lines) and RAI (dashed line) corresponding to the activity indices [K (mass %)] and selectivity indices {[$\sum C_4$], (mass %)} of the electrophilic catalysts $MCl_n \cdot H_2O$ and $[M'MCl_n] \cdot H_2O$ in relation to the thermocatalytic degradation of high pressure polyethylene ($\overline{M}_n = 22\,000$), [Cat] = 1×10^{-3} mol g^{-1}; $T = 623$ K, 1 h. Curves: (*1*) [$\sum C_4$] = $f(pK_a)$; (*2*) [$\sum C_4$] = f(RAI); (*3*) $K = f(pK_a)$; (*4*) $K = f$(RAI).

We may note, however, that in all probability the boundary values of the acidity parameters quoted may shift in the general case in one direction or another depending on the nature of the chemical process, the molecular structure, the solvent employed, etc. evidently mainly in view of the change in situ of the parameters of the acid strength of the electrophilic catalytic system employed.

The acidity of the classical catalysts for electrophilic processes, in particular $AlCl_3$ and BF_3, can be reduced by combining them with moderately basic chlorides of *s* or *d* elements. The class of the relatively new electrophilic catalysts, formed as a result of the interaction of halogen-containing compounds of aluminium with alkali or alkaline earth metal chlorides having the general formula $H[MAlR_nCl_mOH]$, where $n = 0$ or 1 and $m = 4$ or 3 for Na, Li, and K and 5 or 4 for Ca, Ba, Mg, Sr, Zn, Co. etc., is of interest in this connection.

VIII. Conclusion

The Brønsted acids comprising the complexes of Group II – VIII metal chlorides, which have a reduced acidity compared with $AlCl_3$ and are formed, in particular, as a result of the interaction of aluminium chlorides with Group I and II metal chlorides in the presence of proton-donating compounds (H_2O, ROH, etc.), are promising polyfunctional catalysts for many electrophilic reactions, in particular cationic polymerisation processes, the depolymerisation of oligo- and poly-alkenes, the degradation of macromolecules, the alkylation, hydrogenation and dehydrogenation of unsaturated hydrocarbons, the dehydrogenation of alkanes and alicyclic compounds, the desulfurisation (hydrogenolysis) of organosulfur compounds, etc. In the presence of such systems, such reactions proceed fairly selectively with a relatively high degree of conversion and under extremely mild experimental conditions (atmospheric pressure, $T = 270 - 650$ K).

An important factor is that the acidity of the chemical compounds may serve as the criterion determining the electrophilic activity of the catalysts and the selectivity of their action, i.e. their effectiveness. In all probability, by estimating the acidity indices of the catalysts of electrophilic processes, one may predict to a first approximation their effectiveness. The construction of characteristic relations (Figs. 5 and 6) for the series of electrophilic reactions occurring via the carbonium ion mechanism is of extremely great interest in this connection. The observed relations make it possible to estimate the postulated catalytic activity and selectivity of the action of potential electrophilic catalysts, to predict the direction of the changes in the activity and selectivity of the electrophilic catalysts, and to seek on this basis new catalysts for specific electrophilic chemical processes.

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