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The Influence of Ligands on the Catalytic Properties of Nickel-containing Systems in Oligomerisation and Polymerisation Reactions

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The results of studies on the activating influence of ligands on the catalytic properties of nickel-containing systems in oligomerisation, co-oligomerisation, and polymerisation reactions are surveyed and the electronic and steric aspects of this phenomenon are analysed from the standpoint of an S_ECi mechanism. The possibility of a homolytic and heterolytic activation of the Ni-C bond in catalytic centres by electron-accepting and electron-donating ligands respectively is examined. It is shown that the molecular weight of the oligomerisation and polymerisation products is determined by the steric effect of the ligands and that the stability of the catalytic centres depend primarily on the frequency of the active centre ⇌ potential centre transitions.
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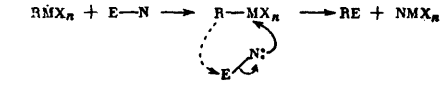
I. INTRODUCTION

In the presence of nickel-containing catalysts it is possible to obtain a broad spectrum of oligomers and polymers of unsaturated hydrocarbons. The composition, structure, and molecular weight of these products depends on the nature of the monomers, the ligand environment of the nickel in catalytic centres, the composition of the catalyst, and the reaction conditions.[1-6] It is now generally recognised that the active centres in nickel-containing catalysts for linear dimerisation, oligomerisation, and polymerisation are in most cases organometallic and hydride derivatives of nickel.[1-7] However, these compounds by themselves exhibit only an insignificant activity. Their catalytic action is greatly enhanced in the presence of electron-accepting additives capable of increasing the effective positive charge on the nickel atom as a result of the formation of charge-transfer complexes on an anion.[1] The influence of electron-donating additives in different reactions is manifested in different ways: they reduce the activity and stereoselectivity of the action of the catalyst in diene polymerisation processes, while in olefin dimerisation and codimerisation reactions they increase its activity and stability.[4-8]

There is as yet no unique approach in the literature to the explanation of the mechanisms of the activating influence of ligands on the catalytic properties of nickel-containing systems in various reactions. This is apparently associated with the fact that, although the studies by individual groups of investigators do cover a broad range of catalytic properties, each separate study was devoted to the investigation of the behaviour of nickel-containing systems only in specific reactions. The mechanisms of the formation and destruction of the active centres, and the role of the electronic and steric factors in the activation of nickel-containing systems and in the formation of the structures and the establishment of the molecular weight of the oligomerisation and polymerisation products have not been ultimately elucidated. The elucidation of these fundamental questions requires a comparative analysis of the activating influence of ligands on the catalytic properties of the same systems in different reactions and, conversely, on different systems in a single standard reaction.

Valuable information about the role of electronic and steric effects of ligands can be obtained by the systematic study of their influence on the kinetic parameters of the elementary stages of the reactions in the transition from dimerisation and codimerisation to oligomerisation and polymerisation of unsaturated hydrocarbons. Evidently, the model reactions should then be selective to the maximum possible extent and readily controllable. The highly selective oligomerisation and co-oligomerisation reactions with α-olefins of styrene and its derivatives, which occupy an intermediate position between olefins and dienes[1,5] as regards their polymer-forming capacities, are convenient objects of study.

In the present review, the experimental data are analysed on the basis of ideas about the electrophilic mechanisms of the reactions of organometallic compounds proceeding via the nucleophilic coordination of the substrate to the metal atom with subsequent electrophilic attack on the negatively charged α-carbon atom in a many-centre cyclic transition state. A similar mechanism, called the S_ECi mechanism was proposed previously,[9] for substitution and addition reactions between organometallic compounds of non-transition metals and E—N electrophiles, which consist of electrophilic (E) and nucleophilic (N) components:



An analogous mechanism can be used also in discussing the reactions involving the addition of unsaturated hydrocarbons to organometallic and hydride derivatives of nickel. These reactions are the key stages in the oligomerisation and polymerisation processes. Indeed, it has now come to be assumed that the addition of unsaturated hydrocarbons to hydride and organometallic centres takes place in two stages: (1) the formation of an intermediate π-complex with the transition metal and (2) the subsequent insertion of the coordinated olefin molecule via a polar cyclic transition state.

According to the Dewar–Chatt–Duncanson model, the binding of olefins to the metal in the π-complexes is achieved as a result of the direct donor–acceptor and the reverse dative interactions.[10,11] The contribution of the dative interaction diminishes with increase of the degree of oxidation of the complex-forming metal and is minimal for high degrees of oxidation of the metal.[12] This means that the π-complex formation processes at the nickel(II)-containing active centres is a nucleophilic reaction in the sense in which it has been considered by Moiseev.[13,14] On the other hand, in the coordinated state, the olefin molecule acquires the capacity for electrophilic attack,[15] because the partial charge appearing on it as a result of the donor–acceptor interaction is not fully compensated by the dative interaction. Under these conditions, in the many-centre transition state the *d* orbitals of the metal and the sp^3 orbitals of the α-carbon atom (or the *s* orbitals of hydrogen) interact with the bonding orbitals of the olefin.[16–18] As a result, the thermal addition reaction is symmetry-allowed or, according to Pearson's terminology, is partly prohibited.[19]

The formal analogy with the S_Ei mechanism is manifested by the fact that the nucleophilic attack on the transition metal atom by the substrate molecule takes place before its electrophilic insertion in the polarised $R^{\delta-}-M^{\delta+}$ bond via an intermediate cyclic transition state. Consequently, one can assume that the characteristics of the reactions involving the addition of an olefin (diene) to organometallic and hydride derivatives of nickel should not differ significantly in their character from the characteristics of the reactions involving the S_Ei mechanism. In this case, the opposite effects of the ligands on the catalytic properties of nickel-containing systems in dimerisation reactions, on the one hand, and in oligomerisation (polymerisation) reactions, on the other, can be accounted for by the different nature of the rate-limiting stages in these processes. Analysis of the experimental results confirms this hypothesis.

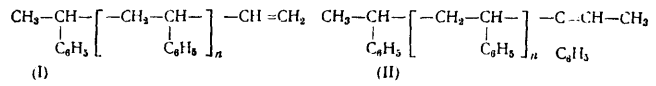
II. THE INFLUENCE OF LIGANDS ON THE MOLECULAR WEIGHT OF OLIGOSTYRENE AND THE CHARACTER OF THE CHAIN TERMINATION IN THE OLIGOMERISATION OF STYRENE

It has been shown[20–23] that the degree of polymerisation of styrene in the presence of π-alkenylnickel halides depends on the nature of the halide ion. Thus π-crotylnickel iodide induces the formation of the styrene dimer (1,3-diphenylbut-1-ene), while the bromide and chloride complexes lead to the formation of oligostyrenes with average degrees of polymerisation of 5–6 and 8–12 respectively. An even greater increase in the length of the chain (up to 200–500 units) is attained when electron acceptors such as $MnCl_2$ and $Ni(OCOCCl_3)_2$ are introduced into the system.[22]

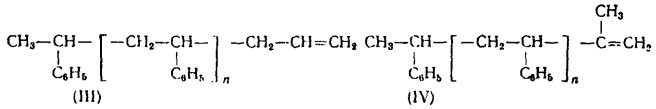
The molecular weight of the styrene oligomerisation products in the presence of systems of the Ziegler–Natta type also depends on the catalyst.[24] The two-component system containing *NN*-diethyldithiocarbamate or nickel *OO*-dialkyl (or *OO*-diaryl) phosphorodithioate and diethylaluminium chloride directs the process towards the formation of a dimer, while the additional introduction of a phosphorus-containing ligand (phosphine, phosphite) results in the formation of oligomers with an average degree of polymerisation of 4–9. This difference between the two- and three-component systems is due to the change in the character of chain termination in the presence of a phosphorus-containing ligand in the coordination sphere of nickel: instead of spontaneous chain transfer (β-elimination), the chain is transferred to the monomer, which increases the average degree of polymerisation. Comparison of the results of Azizov et al.[25] with the data of Makovetskii and co-workers[20–22] shows that the introduction of both electron-accepting and electron-donating ligands can increase the molecular weight of the styrene oligomerisation products.

III. THE SELECTIVITY OF THE CO-OLIGOMERISATION REACTIONS OF STYRENE WITH ETHYLENE AND PROPENE

In the co-oligomerisation of styrene with α-olefins, the latter add "head to tail" and "tail to tail". The structure of the products of the reaction with participation of ethylene corresponds to formulae (I) and (II) and that of the products of the reaction involving propene corresponds to formulae (III) and (IV):



(I) (II)



(III) (IV)

The products (I)–(III) are formed as a result of the "head to tail" addition, while the product (IV) results from the "tail to tail" addition. In the limiting case, where $n = 0$, the product of the co-oligomerisation of styrene with ethylene is 3-phenylbut-1-ene and those of the co-oligomerisation with propene are 4-phenylpent-2-ene, 4-phenylpent-1-ene, and 2-methyl-3-phenylbut-1-ene (2-M-3-PB-1).[25,26]

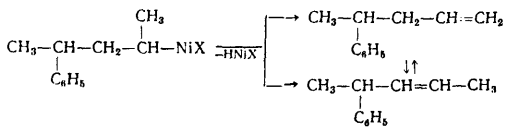
In contrast to the codimerisation of other pairs of the lowest olefins (for example, ethylene and propene[4,5,7]), in the codimerisation of styrene with ethylene[19] only a single product, namely 3-phenylbut-1-ene, is formed up to appreciable degrees of conversion. For very high conversions, 2-phenylbut-1-ene isomerises to 2-phenylbut-1-ene. The curve for the accumulation of 3-phenylbut-1-ene as a function of time therefore passes through a maximum, which corresponds to 80–100% conversion of styrene.[8,19] The nature of the components of the catalytic system has a considerable influence on the process selectivity. The highest yield of 3-phenylbut-1-ene (100%) is observed in the presence of catalytic systems based on organic dithio-derivatives of nickel (dithiocarbamate, phosphorodithioate).[24,27] The dimerisation of ethylene in the presence of a tertiary phosphine or a phosphite in the catalyst is appreciable only for a high degree of conversion of styrene (>90%). When a two-component system is used, the yield of 3-phenylbut-1-ene falls sharply with respect to both monomers which have reacted (it is particularly marked with respect to the ethylene which has reacted) compared with the three-components systems.[8,25,28] 3-Phenylbut-1-ene isomerises after the complete conversion of styrene.

The yields of the reaction products pass through a maximum also in the codimerisation of *p*-chlorostyrene and vinyltoluene with ethylene. On the other hand, in the codimerisation of α-methylstyrene with ethylene isomerisation is not

observed and the yield of 3-methyl-3-phenylbut-1-ene corresponds fully to the consumption of α-methylstyrene.[25]

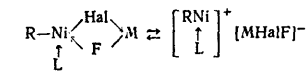
The codimerisation of styrene with propenes takes place both "head to tail" and "tail to tail". The former type leads to the formation of a mixture of 4-phenylpentenes and the latter to the formation of 2-methyl-3-phenylbut-1-ene. In certain cases propene dimers, phenyloctenes, and styrene oligomers are also formed.[27-30] In the given case the selectivity of the codimerisation also depends, other conditions being equal, on the nature of the components and on the composition of the catalyst: in the presence of two-component systems, an appreciable amount of styrene (up to 42%) is converted into oligomers and co-oligomers. Dithio-systems ensure the exclusive formation of codimers—phenylpentenes (PP). Up to the complete conversion of styrene, they catalyse the addition of the monomers of the "head to tail" type only and, in contrast to acetylacetonate systems, the increase of the Al:Ni ratio to 200:1 does not lower the selectivity of their action.[29,30]

Regardless of the nature of the catalyst components, the 4-PP-1 and 4-PP-2 codimers are formed from the very beginning of the process, which is consistent with the hypothesis of their formation from the same intermediate as a result of β-elimination reactions via different pathways:



However, the isomerisation of 4-PP-1 to 4-PP-2 also takes place during the process. The isomerisation continues further after the formation of 2-PP-2. In contrast to 4-PP-1, 4-PP-2 isomerises to 2-PP-2 only after the complete conversion of styrene. This fact, together with the low rate of isomerisation of 3-phenylbut-1-ene, indicates a decrease of the rate of isomerisation as the double bond is located closer to the benzene ring. Comparison of the results of a thermodynamic calculation of the equilibrium composition of phenylpentenes with experimental data leads to the same conclusion.[29,30] Regardless of the nature of the catalyst components, the yield of 4-PP isomers for any degree of conversion of styrene greatly exceeds their maximum equilibrium concentrations, which are 0.1% for 4-PP-1, 72% for *trans*-4-PP-2, and 15% for *cis*-4-PP-2 at 10–50 °C. With increase of the degree of conversion, the content of 4-PP-1 in the codimerisation products diminishes, approaching the equilibrium value, while that of 4-PP-2 increases to 50–95 wt.%. The yield of 2-PP-2 (1–9%) is much smaller than the theoretical value (28–94%), which is due to the slow isomerisation of 4-PP-2.

The nature of the organoaluminium compound has a significant influence on the yield of the codimerisation products.[27] Catalytic systems based on triethylaluminium and not containing activating additives have a very low efficiency. When CH_2Cl_2, $AlCl_3$, $TiCl_4$, $BF_3.(C_2H_5)_2O$, and $C_2H_5AlCl_2$ are introduced into such systems, the rate of the process and the overall yield of the codimerisation products increase sharply, indicating that the most active codimerisation centres contain electron-accepting ligands or the products of their interaction with the organoaluminium compounds. This postulate is confirmed by the results of studies[31,32] of the interaction of the components of the $Ni(acac)_2 + P(OC_6H_5)_3 + Al(C_2H_5)_3$ and $Ni(acac)_2 + P(OC_6H_5)_3 + Al(C_2H_5)_3^{\ddagger} + BF_3(C_2H_5)_2O$ catalytic systems in solution in halogenohydrocarbons. The oxidative addition of the halogenohydrocarbon to the intermediate complexes results in the formation in the system of organometallic nickel complexes of the type



where M = B or Al, L = phosphorus-containing ligand, and X = halide ion.

The nature of the activating ligand influences also the composition of the codimerisation products. Chlorine-containing compounds direct the process towards the preferential formation of 4-PP-2.[27] In the presence of boron trifluoride etherate, the reaction products contain a large amount of 4-PP-1. Catalytic systems containing $Al(C_2H_5)_2Cl$ exhibit a high activity without electron-accepting additives and the isomeric composition of the phenylpentenes depends in this case on the nature of the electron-donating ligand and the P:Ni ratio. For the ratio P:Ni = 1, 2-methyl-3-phenylbut-1-ene, the product of the "tail to tail" addition (yield up to 15%), is present among the reaction products together with 4-phenylpentenes. The increase of the P:Ni ratio to 4:1 or the replacement of the phosphorus-containing ligand by bipyridyl fully suppresses the "tail to tail" addition. The main reaction product is then 4-PP-2 (95–96%). In the absence of electron-donating ligands, a large amount of styrene oligomerises, which reduces the yield of phenylpentenes.[27,29,30]

Thus the introduction of phosphorus-containing ligands into the coordination sphere of nickel increases the selectivity of the codimerisation of styrene with ethylene and propene. The most active catalytic centres contain electron-accepting acido-ligands and neutral ligands. The nature of the acido-ligand in the initial nickel compound has a significant influence on the activity and selectivity of the action of nickel-containing systems of the type of Ziegler–Natta catalysts, which indicates the retention of the bond between this ligand and nickel in the catalytic centres. This is also indicated by the results of kinetic studies.[8,24,27,29,30-33]

IV. GENERAL KINETIC FEATURES OF THE STYRENE OLIGOMERISATION AND CO-OLIGOMERISATION REACTIONS

The orders of the oligomerisation and co-oligomerisation with respect to the monomers depend on the nature of the components, the composition of the catalytic systems, and the reaction temperature. In the dimerisation of styrene in the presence of the nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride two-component system, the reaction order depends on temperature and varies from 0.43 to 0.95 in the range 10–33 °C. When triphenyl phosphite is introduced into the catalyst, the reaction order with respect to styrene becomes unity and is independent of temperature but the molecular weight of the oligostyrene is then found to increase.[24]

A change in reaction order is observed also in the codimerisation reactions of styrene or α-methylstyrene with ethylene and propene.[8,28-30,33] In this case, the rates of formation of the codimers obey the complex relation $v = K[\text{catalyst}][\text{styrene}]^n[\text{olefin}]^m$, where K is the codimerisation rate constant and n and m depend on the nature and concentration of the olefin, the nature of the catalyst components, and temperature, varying in the range from 0 to 1 (Table 1). Thus, in the codimerisation of styrene with ethylene in the presence of the $Ni(acac)_2 + P(OC_6H_5)_3 + Al(C_2H_5)_3 + BF_3(C_2H_5)_2O$ catalytic system, which exhibits a

moderate activity, at −30 °C the rate of formation of 3-phenylbut-1-ene is almost independent of both the initial styrene concentration and time, i.e. $n = m = 0$.[32]

Table 1. The orders of the codimerisation reactions of styrene and α-methylstyrene with ethylene.

Catalytic systems*	T, °C	Reaction order w.r.t. styrene or α-methylstyrene	Reaction order w.r.t. ethylene	Refs.
Styrene				
Ni (acac)$_2$ P (OC$_6$H$_5$)$_3$ + (C$_2$H$_5$)$_3$ Al + + BF$_3$·(C$_2$H$_5$)$_2$O, where Ni:P:Al:B = 1:1:3:5	−30 5 15 25 **	0 0.7 — 1.0	0.7 0 7 0.9 1,0	[33]
Ni (acac)$_2$ + Li + (C$_2$H$_5$)$_3$ Al + BF$_3$·(C$_2$H$_5$)$_2$·O, where Ni:bipy:Al:B = 1:1:3:5	25	0	0.4	[33]
Ni (acac)$_2$ + P (OC$_6$H$_5$)$_3$ + (C$_2$H$_5$)$_2$ Al, where Ni:P:Al = 1:1:100	−30 −20	0 0	— —	[33]
Ni(DEDTC)$_2$ + P(OC$_6$H$_5$)$_3$ + (C$_2$H$_5$)$_2$AlCl, where Ni:P:Al = 1:1:100	−20 −10 2 **	0 0 0	— —	[8]
Ni(DEPDT)$_2$ + P(OC$_6$H$_5$)$_3$ + (C$_2$H$_5$)$_2$AlCl, where Ni:P:Al = 1:1:100	−20 −10 2 ** 10	0 0 0 0	— — — —	[8]
α-Methylstyrene				
Ni(DPPDT)$_2$ + (C$_2$H$_5$)$_2$AlCl, where Ni:Al = 1:100	−10 2 10	0 0 0	— — —	[8]
Ni (acac)$_2$ + P (OC$_6$H$_5$)$_3$ + (C$_2$H$_5$)$_3$ Al + + BF$_3$ (C$_2$H$_5$)$_2$ O, where Ni:P:Al:B = 1:1:3:5	25 15 5	0,8 0 0	0.9 — 0.7	[33]

*DEDTC = diethyldithiocarbamate, DEPDT = diethyl phosphorodithioate, DPPDT = diphenylphosphorodithioate, and bipy = bipyridyl.
** The reaction order with respect to nickel is 1.

An analogous behaviour has been observed also in the codimerisation of α-methylstyrene with ethylene at 15 °C.[33] With increase of temperature to 25 °C, there is a transition from the zero reaction order with respect to α-methylstyrene to the first order process. When phosphite in the catalyst is replaced by αα′-bipyridyl, the zero order with respect to styrene is retained also at 25 °C. The same reaction order is observed also in the presence of highly active catalytic systems containing organic dithio-derivatives of nickel (dithio-systems).[8,29,30] The reaction order with respect to ethylene likewise depends on temperature and, when the reaction order with respect to styrene (or α-methylstyrene) is zero, it is less than unity, while under the conditions where the rate of codimerisation is directly proportional to the styrene concentration the order with respect to ethylene is also unity. At a methylene pressure above 0.3 MPa, the rate of codimerisation in the presence of the dithio-systems is independent of the styrene and ethylene concentrations.[8]

In the codimerisation of styrene with propene, the reaction order with respect to propene in the range of concentrations of the latter 1–7 M is independent of the nature of the catalyst and is close to unity, while the order with respect to styrene varies from 0 to 1 (Table 2). Depending on the nature of the catalyst components, the kinetic curves can be S-shaped or can be straight lines, the latter being observed in the presence of three-component dithio-systems.[27,29,30] Linear kinetic plots imply that in the presence of these systems the rate of codimerisation does not change when the concentrations of the monomers are varied with time, i.e. in this case a zero reaction order with respect to both monomers is attained.

V. DEPENDENCE OF THE FORM OF THE KINETIC EQUATIONS FOR THE OLIGOMERISATION AND CO-OLIGOMERISATION OF STYRENE ON THE NATURE OF THE LIGANDS

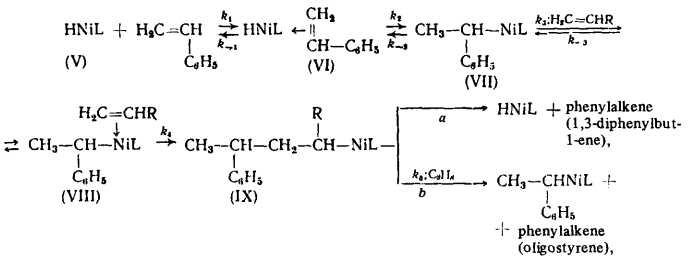
A common stage in the processes involving the oligomerisation of styrene and its codimerisation with olefins is the addition of the first styrene molecule to nickel hydride. The second monomer added in oligomerisation is again styrene, while in co-dimerisation it is ethylene or propene. The dependence of the reaction order with respect to the reacting monomers on the nature of the catalyst components and the experimental conditions indicates in general the equilibrium character of the stages in which the monomers are added to the active centres and confirms the two-stage nature of

Table 2. The orders of the codimerisation reaction of styrene with propene with respect to the monomers.[29,30]

Catalytic system	T, °C	2-M-3-PB-1		4-PP-1		4-PP-2		Sum of codimers	
		n	m	n	m	n	m	n	m
Ni(acac)$_2$ + bipy + (C$_2$H$_5$)$_2$AlCl	23	—	—	0	1,24	0	1,11	0	1 0
Ni (acac)$_2$ + P (OC$_6$H$_5$)$_3$ + (C$_2$H$_5$)$_3$ AlCl	23	0.90	1.10	0.92	1.10	1.20	1.17	1.04	1.08
Ditto	2	1.30	0.77	1.08	1.14	0.89	1.11	1 00	0.82
Ni (acac)$_2$ + P (OC$_6$H$_5$)$_3$ + (C$_2$H$_5$)$_2$ AlCl	23	0.80	0.85	0.80	0.70	0.90	1.14	0.98	1 17
Ni (acac)$_2$ + P (O—CH$_3$C$_6$H$_4$O)$_3$ + + (C$_2$H$_5$)$_2$ AlCl	23	0.87	1.20	0.90	1.20	1.00	0.92	1.10	0.88
Ni(DPPDT)$_2$ + P(OC$_6$H$_5$)$_3$ + + (C$_2$H$_5$)$_2$ AlCl	2	—	—	0	1.07	0	1.10	0	1.10
Ni(DEDTC)$_2$ + P(OC$_6$H$_5$)$_3$ + + (C$_2$H$_5$) AlCl	2	—	—	0	0.95	0	1.00	0	1.00
Ni(DEDTC)$_2$ + P(OC$_6$H$_5$)$_3$ + + (C$_2$H$_5$)$_2$ AlCl *	2	—	—	0	1.00	0	1.06	0	1.04

*Catalyst prepared in the presence of styrene.

this reaction (the presence of coordination and insertion stages):



where R = C_6H_5 in oligomerisation and R = H or CH_3 in codimerisation.

It has been shown[29,30,33] that the rate of codimerisation is satisfactorily described by the general kinetic equation

$$v_1 = \frac{\alpha\beta k_4 K' K'' K''' [\mathrm{Ni}]_0 [\mathrm{St}]_0 p}{1 + (K' + K'K'' + \beta K'K''K''' p)[\mathrm{St}]_0} \quad (1)$$

and when the reaction order with respect to styrene is zero by the equations

$$v_1 = \frac{\alpha\beta k_4 K' K'' K''' [\mathrm{Ni}]_0 p}{K' + K'K'' + \beta K'K''K''' p} \quad (2)$$

$$v_2 = \frac{\alpha\beta k_3 k_4 k_5 [\mathrm{Ni}]_0 p}{(k_{-3} + k_4) k_5 + (k_4 + k_5)\beta k_3 p} \quad (3)$$

where v_1 and v_2 are the rates of formation of the codimers via pathways *a* and *b* respectively, α is the fraction of active codimerisation centres relative to the initial concentration of the nickel compound, β the solubility coefficient of the olefin, k_3, k_{-3}, k_4, k_{-4}, and k_5 are the rate constants for the corresponding elementary stages, K', K'', and K''' the stability constants of the complexes (VI), (VII), and (VIII) respectively, p is the olefin pressure, and $[\mathrm{Ni}]_0$ and $[\mathrm{St}]_0$ are the initial concentrations of the nickel compound and styrene respectively.

For zero order with respect to both reacting monomers, the rate of codimerisation via pathway *b* obeys the equation[8]

$$v_2 = \frac{\alpha k_4 k_5 [\mathrm{Ni}]_0}{k_4 + k_5} \quad (4)$$

or, when $k_5 \geq k_4$, the equation

$$v_2 = \alpha k_4 [\mathrm{Ni}]_0 \quad (5)$$

When the reaction order with respect to styrene is zero and that with respect to olefins is unity, we have

$$v_1 = \frac{\alpha\beta k_4 K' K'' K''' [\mathrm{Ni}]_0 p}{K' + K'K''} \quad (6)$$

$$v_2 = \frac{\alpha\beta k_3 k_4}{k_{-3} + k_4} [\mathrm{Ni}]_0 p \quad (7)$$

If $k_{-3} \gg k_4$, then according to Eqn.(7) the effective codimerisation rate constant $k_{\mathrm{eff}} = \alpha\beta k_4 K'''$, i.e. it depends both on the stability constant K''' and on the rate constant k_4 for the insertion stage. If the temperature coefficient of the constant K''' is then low, the activation energy for the overall codimerisation process is determined mainly by the activation energy for the insertion stage. On the other hand, if $k_{-3} \ll k_4$, then $k_{\mathrm{eff}} = \alpha\beta k_3$ and the activation energy is determined by the temperature dependence of the rate constant for the complex formation stage. Usually $k_{-3} \gg k_4$ in the codimerisation of styrene with ethylene and propene,[8,29,30,33] while in the oligomerisation of styrene we have the opposite situation with $k_{-3} \ll k_4$.[27-29] Consequently the first order of the oligomerisation reaction is a consequence of an appreciable contribution by the complex formation step in the propagation stage to the overall process kinetics. The effective rate constant for chain propagation in then identical with the complex formation rate constant.[8] The experimental results are described satisfactorily by the equation[24]

$$v_d = \frac{\alpha k_1^* k_2^* k_3^* [\mathrm{Ni}]_0 [\mathrm{St}]_0}{k_3^* (k_1^* + k_2^*) + k_1^* k_2^* [\mathrm{St}]_0} \quad (8)$$

$$v_{ol} = \alpha(k_p^* + k_t^*)[\mathrm{Ni}]_0 [\mathrm{St}]_0, \quad (9)$$

$$\bar{P}_p = \frac{k_p^*}{k_t^*} + 1, \quad (10)$$

where v_d and v_{ol} are the rates of dimerisation and oligomerisation of styrene respectively, $\bar{P}_p$ is the average degree of polymerisation of styrene, k_1^* and k_2^* are the effective rate constants for the stages involving the addition of the first and second molecules of styrene in dimerisation, k_3^* is the effective rate constant for the elimination of the dimerisation product (1,3-diphenylbut-1-ene) from the complex (IX), and k_p^* and k_t^* are the effective rate constant for chain propagation and chain transfer to the monomer in the oligomerisation of styrene. The remaining notation was explained above.

VI. KINETIC PARAMETERS OF THE ELEMENTARY STAGES IN THE STYRENE OLIGOMERISATION AND CO-OLIGOMERISATION PROCESSES

Eqns.(1)–(10) and their forms in terms of the variables $1/v_i$ and $1/[\mathrm{M}]$, where v_i is the rate of formation of the *i*th produce and [M] the concentration of one of the reacting monomers, make it possible to determine the rate constants for the elementary stages or their combinations and to estimate how they vary as a function of the nature of the components and the composition and conditions governing the preparation of the catalyst.

The kinetic parameters of the dimerisation and oligomerisation of styrene calculated with the aid of Eqns.(1)–(3) have been published.[24] The introduction of a phosphorus-containing ligand into the catalyst increases the activation energy for chain propagation (39 kJ mol^{-1} in the two-component system and 58–63 kJ mol^{-1} in the three-component system). At the same time, as shown above, the character of the chain termination changes on passing from dimerisation to oligomerisation: instead of the β-elimination of nickel hydride, chain transfer to the monomer takes place. The activation energy for chain termination then changes little but the ratio of the chain propagation and chain termination rate constants increases, which ultimately promotes the formation of an oligomer with a high molecular weight.[24]

Phosphorus-containing ligands exert the opposite influence on the activation energy for the codimerisation of styrene with ethylene.[8,28] On passing from the two-component to the three-component system, the activation energy for codimerisation falls sharply (almost by a factor of two), while the rate constant increases by a factor greater than 10.

The kinetic parameters change also in the codimerisation of styrene with propene:[29,30] depending on the nature of the catalyst components, the activation energy E_a ranges from 29–33 to 63–64 kJ mol^{-1}. It decreases on passing from the two-component to the three-component system and from the acetylacetonate system to the dithio-system. The activation energy for the formation of 4-PP-2 is in all cases greater than that for the formation of 4-PP-1 (by 8–16 kJ mol^{-1}). However, the rate of formation of 4-PP-2 is higher than the

rate of formation of 4-PP-1 even along the initial sections of the kinetic curves, where the degree of isomerisation of 4-PP-1 to 4-PP-2 is very low.[27,29,30,34] Hence it follows that at least in the initial instant 4-PP-1 and 4-PP-2 are formed on different centres, the centres for the formation of the second isomer predominating.

The opposite influence of phosphorus-containing ligands on the activation energies for styrene oligomerisation and codimerisation processes is a direct consequence of the different nature of the rate-limiting stages in these processes. The presence of a phosphorus-containing ligand in the coordination sphere of nickel diminishes the activation energy for the insertion stage and increases that for the olefin coordination stage.

Table 3. Kinetic parameters of the polymerisation of butadiene.[1,35,37,38]

Catalytic system	T, °C	N_p, %	k_p, litre mol^{-1} min^{-1}	k_d, litre mol^{-1} min^{-1}	Activation energy***, kJ mol^{-1}	
					E_p	E_d
$(C_4H_7NiCl)_2$ – dichloroquinone	20	7	11	44	33.4	20.6
	30	7	18	58		
	50	8	40	98		
$(C_4H_7NiCl)_2$ – chloranil*	0	10	12	30	26.0	15.7
	10	9	20	36		
	20	9	27	50		
	30	8.5	46	63		
	40	—	58	73		
$(C_4H_7NiCl)_2$ – fluoranil	7	16	32	46	30.0	17.0
	20	17	49	67		
	30	17	85	82		
C_3H_5NiCl – chloranil	22	—	153	80	—	—
$[(C_2H_5O)_2PS_2]_2Ni$ – $(C_2H_5)_2AlCl$**	15	44	437	349	30.5	49.7
	25	36	898	1076		
	35	28	967	1376		
	45	20	1415	3028		

* The rate constants for the chain transfer to the monomer (k_t^M/k_p) and to the catalyst (k_{cat}/k_p) at 25 °C are $k_t^M/k_p = 2 \times 10^{-4}$ and $k_{cat}/k_p = 5 \times 10^{-3}$.

** $k_t^M/k_p = 1.3 \times 10^{-2}$ and $k_{cat}/k_p = 1.1 \times 10^{-2}$.

*** The activation energy for the polymerisation of butadiene in the presence of pure π-alkenylnickel is 60–70 kJ mol^{-1},[1] while in the presence of the $[(C_2H_5O)_2PS_2]_2Ni$ + bipyridyl + $(C_2H_5)_2AlCl$ catalytic system it amounts to 56.2 kJ mol^{-1}.[37]

VII. KINETIC PARAMETERS OF THE ELEMENTARY STAGES OF THE POLYMERISATION OF BUTADIENE

The dependence of the kinetic parameters of the elementary stages of the process on the nature of the ligands can be traced in relation to the polymerisation of butadiene in the presence of catalytic systems of three different types: π-alkenylnickel chloride + quinones,[35,36] nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride, and nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride + bipyridyl.[37,38] The kinetic constants were calculated from the rates and degrees of polymerisation with the aid of the corresponding kinetic equations. The initial concentrations of the chain propagation centres in the π-alkenyl systems were estimated from the initial concentration of the growing chains.[36] The standard deviation of the calculated values of the parameters listed in Table 3 from the experimental values was less than 3%.

Table 3 shows that the concentration of the propagation centres N_p is in all systems less than the initial concentration of the nickel compound, amounting to not more than 44% of $[Ni]_0$ depending on the nature of the catalyst components and the experimental conditions. In the case of the dithio-system, the calculated maximum concentration of the propagation centres diminishes with increase of temperature, which is due to their bimolecular deactivation.[37,38] The activation energy for the destruction of the centres E_d in this system exceeds that for the chain propagation E_p by ~18 kJ mol^{-1}. In the presence of an electron-donating ligand (bipyridyl), a sharp increase of the process activation energy is observed.[37]

The introduction of electron-accepting ligands (quinones) into π-alkenyl systems tends to decrease the activation energy for polymerisation.[1] Both the propagation rate constants k_p and the bimolecular deactivation rate constants k_d increase on passing from a weaker π-electron acceptor (dichloroquinone) to a stronger acceptor (chloranil, fluoranil), while the corresponding activation energy diminishes under these conditions.

The stronger activating effect of fluoranil (compared with chloranil) is a consequence of the increased concentration of the propagation centres and the high activation energy for chain propagation (25–30 kJ mol^{-1}), while the difference between the electron affinities of these quinones is small (the half-wave potentials for chloranil and fluoranil are respectively +0.01 and −0.04 V).[35,36]

The presence in the catalyst of a strongly nephelauxetic dithio-ligand[39] increases appreciably (by two orders of magnitude and above) the rate constants for the elementary stages compared with powerful π-electron acceptors such as halogenoquinones. However, this increase is achieved by virtue of the more favourable steric conditions and not as a result of the decrease of the activation energy, because the E_a in the highly active dithio-system either differs little from the E_a in the π-alkenylnickel chloride + quinone systems or exceeds it (cf. E_p and E_d in Table 3).

As for the π-alkenyl systems, one of the principal chain termination reactions in the presence of dithio-systems is chain transfer to the monomer. However, the rate constant for this last stage in the presence of dithio-systems is higher by two orders of magnitude, which causes the formation of low-molecular-weight polybutadiene,[37] while the less active π-alkenyl systems lead to the formation of high-molecular-weight polybutadiene.[1]

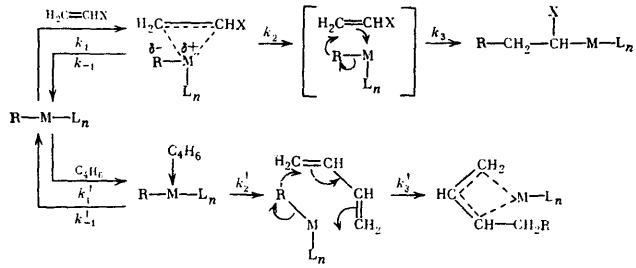
Thus, in the polymerisation of butadiene electron-accepting ligands diminish the activation energy for the chain propagation stage, while electron-donating ligands increase it. The molecular weight is determined not so much by the steric characteristics of the ligands as by their energetic (electronic) characteristics.

VIII. THE S_ECi MECHANISMS OF THE CATALYTIC ACTION OF NICKEL-CONTAINING SYSTEMS. THE ROLE OF ELECTRONIC AND STERIC PROPERTIES OF THE LIGANDS

The study of the influence of various electron-donating and electron-accepting ligands on the activity and selectivity of nickel-containing systems in dimerisation, codimerisation, oligodimerisation, and polymerisation processes and also on the kinetic parameters of these reactions has shown that electron-accepting ligands as a rule tend to decrease the acti vation energy and to increase the rate of the process. The

influence of electron-donating ligands in various reactions is manifested in different ways: they increase the activation energies for the oligomerisation of styrene and the polymerisation of butadiene, while they decrease the activation energy for the codimerisation of styrene with ethylene and propene.

The results obtained make it possible to regard the elementary stage involving the addition of the monomer to the catalytic hydride or organometallic centre as an electrophilic reaction proceeding via a stage in which the monomer undergoes nucleophilic coordination to the metal (Abraham's $S_E Ci$ mechanism):[9]



where R = H, alkyl, benzyl, or alkenyl and L_n = set of remaining ligands.

This approach makes it possible to classify the catalytic mechanisms of nickel-containing systems in linear oligomerisation and polymerisation processes in terms of the kinetic features of the reactions and the electronic effects of the ligands from a single standpoint and to explain the causes of the opposite influence of the introduction of phosphorus-containing ligands on the activation energies for various processes.

According to these ideas, in those cases where the rate-limiting stage is the nucleophilic coordination of the monomer to the metal, the introduction of an electron-donating ligand into the coordination sphere of nickel increases the activation energy for the process. On the other hand, if the electrophilic insertion of a coordinated monomer molecule becomes the rate-limiting stage, then electron-donating ligands tend to decrease the activation energy, apparently as a consequence of the increase under their influence of the electron density at the α-carbon atom in the Ni–C bond. The activation of the system reacting via the first mechanism takes place under the influence of electron-accepting ligands, while the presence of electron-donating ligands is essential for the activation of systems reacting via the second mechanism. The first type of activation is manifested in styrene oligomerisation reactions[31,32] and also in the polymerisation of butadiene.[1,40–42] The codimerisation reactions of styrene with ethylene and propene are examples of activation of the second type.[8,29,30]

The styrene oligomerisation and co-oligomerisation reactions then proceed via different versions of the $S_E Ci$ mechanism, which differ by the nature of the rate-limiting stages and correspondingly by the overall orders with respect to the reactants.

Investigations have shown that the overall kinetic features of the dimerisation, oligomerisation, and polymerisation reactions in the presence of nickel-containing systems vary within wide limits, so that the rates of the overall processes can be described by first-, second-, third-, and fractional-order kinetic equations.[8,24,29,30,33,35,36] In terms of the $S_E Ci$ mechanism, the corresponding versions can be classified as the $S_E 1Ci$, $S_E 2Ci$, $S_E 3Ci$, and $S_E nCi$ mechanisms.

Such mechanisms obtain when the nucleophilic coordination of the monomer is a rapid non-equilibrium process and the kinetics of the overall reaction is determined by the electrophilic insertion stage. The effective rate constant is then identical with the overall rate constant for the insertion process. A characteristic feature of the $S_E 1Ci$ mechanism is the independence of the rate of the process of the concentrations of the reacting monomers. The activation of systems acting via the $S_E 1Ci$ mechanism is possible when electron-donating ligands, increasing the heteropolar character of the $R^{\delta-}-M^{\delta+}$ bond, are introduced into the coordination sphere of the metal. This is achieved by reducing the activation energy for the insertion stage. Examples of the $S_E 1Ci$ mechanism are provided by the codimerisation reactions of styrene with ethylene and propene in the presence of dithio-systems.

The $S_E 2Ci$ mechanism is determined by the contribution of the nucleophilic coordination of the monomer to the overall process kinetics, whereupon the effective rate constant is either equal to the complex formation rate constant ($k_{eff} = k_1$) or represents a combination of the rate constants for elementary stages (for example, $k_{eff} = k_1 k_2 / k_{-1}$, where k_2 is the overall rate constant for the insertion stage). When the equality $k_{eff} = k_1$ holds, the process activation energy increases in the presence of electron-donating ligands, which diminish the effective positive charge on the metal and thereby retard the nucleophilic monomer coordination stage, which determines the overall rate of reaction. In order to increase the efficiency of the catalytic action of the system, it is essential to introduce electron-accepting, neutral and nephelauxetic acido-ligands into the coordination sphere of the metal. The introduction of these ligands increases the effective positive charge on the metal as a result of the formation of inner-sphere π-bonds or bridging σ-bonds (M...X...L) and also anisotropic or outer-sphere complexes with transfer of charge (and the anion), which ultimately diminishes the process activation energy. Such influence of the ligand is characteristic of styrene oligomerisation and butadiene polymerisation processes. If $k_{eff} = k_1 k_2 / k_{-1}$, then the introduction of electron-donating ligands into the coordination sphere of the metal decreases the process activation energy, because the stage involving the electrophilic insertion of the coordinated monomer molecule becomes rate-determining. This version of the $S_E 2Ci$ mechanism operates in the codimerisation of styrene with ethylene and propene in the presence of acetylacetonate systems. Apart from the first order with respect to the monomer, its characteristic feature is the decrease of the process activation energy after the introduction of electron-donating ligands into the catalyst.[29,30,33]

The $S_E 3Ci$ mechanism is manifested when the effective rate constant for the process includes the rate constants (or equilibrium constants) for the nucleophilic stages in which two molecules of the same monomer or the molecule of different monomers are coordinated (for example, $k_{eff} = K' K'' k_2$, where K' and K'' are the stability constants of the π-complexes incorporating one and two molecules of identical or different monomers respectively and k_2 is the insertion rate constant). The addition of two molecules can take place either consecutively or simultaneously, while the insertion of one molecule is accompanied by the reversible coordination of another. The principal distinctive feature of this mechanism is the overall second order with respect to the reacting monomers (monomer) and the first order with respect to the catalyst. The influence of electron-donating and electron-accepting molecules on the process activation energy is the same as in the $S_E 2Ci$ mechanism. This case obtains in the codimerisation of styrene with ethylene and propene in the presence of acetylacetonate systems at elevated temperatures (>15 °C). It apparently occurs also in many other instances of the homo- and co-oligomerisation of olefins and also in polymerisation under the influence of metal

complex systems when the overall order with respect to the monomer is two.[1,4]

The $S_E nCi$ mechanism occupies an intermediate position between the $S_E 1Ci$ and $S_E 2Ci$ mechanisms or between the $S_E 2Ci$ and $S_E 3Ci$ mechanisms. It obtains when the contributions of the nucleophilic and electrophilic components in the $S_E Ci$ addition are comparable. The effective process rate constant is a complex combination of rate constants and at least one of the terms in the denominator of the rate equation includes the monomer concentration [for example, Eqns. (1), (2), and (8)]. A characteristic feature of this mechanism is the fractional overall order with respect to the monomers ($1 < n < 2$ or $2 < n < 3$). The temperature dependence of the reaction orders with respect to the monomers must be regarded as a second characteristic feature. The activating influence of the ligands on the properties of catalytic systems is in this case indefinite. It depends on the ratio of the rate constants for the nucleophilic and electrophilic stages in the $S_E Ci$ addition. In particular, electron-donating ligands can both decrease and increase the process activation energy or they may not influence it at all. The $S_E nCi$ mechanism is apparently encountered more often than the other mechanisms. It can be clearly traced in the styrene dimerisation reactions and in the codimerisation of styrene with ethylene and propene and is apparently also observed in diene polymerisation reactions.[1,8,24,29,30]

The proposed classification of the mechanisms of catalytic action make it possible to make sense of the wide variety of kinetic features observed in the linear oligomerisation and polymerisation processes catalysed by nickel-containing and other systems. It helps in many respects to predict the mechanisms of the activating action of ligands and to understand the causes of opposing influences on the catalytic efficiency of systems in various ologomerisation and polymerisation reactions. The influence of polar solvents on the rate of catalytic processes can be satisfactorily explained from the standpoint of the $S_E Ci$ mechanisms: highly basic solvents (ethers, sulphides, amines) hinder the nucleophilic coordination of the monomer, competing with the latter for the inner coordination sphere of the metal, while halogenohydrocarbons, capable of forming anisotropic or outer-sphere charge-transfer complexes, accelerate it. This leads ultimately to an increase in the rate of the process, which has been demonstrated for the codimerisation of styrene with ethylene.[8]

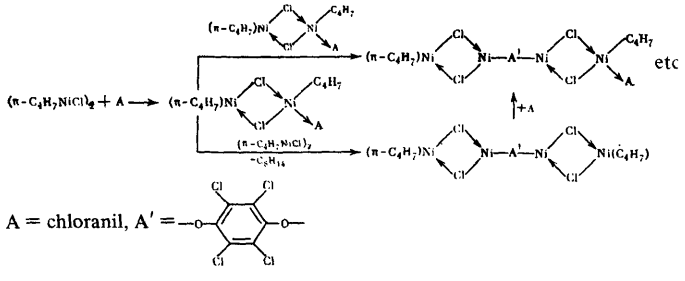
The changes, not only in the rate of polymerisation of butadiene, but also in the stereospecificity of the catalytic action of the systems under the influence of electron-donating and electron-accepting additives can be explained in terms of the $S_E Ci$ mechanisms. In the presence of electron-donating ligands in the coordination sphere of the metal, the rate of the nucleophilic coordination of the monomer is diminished, on the one hand, and the probability of such coordination of the penultimate unit, which fixes the terminal unit in the *anti*-configuration, decreases, on the other hand. The $\pi-\sigma$ and *anti–syn* isomerisation processes in the terminal unit are then facilitated, which is also promoted by the increase of the heteropolar character of the $M^{\delta+}-C^{\delta-}$ bond. As a result, the polymer microstructure shifts towards the 1,4-*trans*-configuration of the units. On the other hand, in the presence of electron-accepting ligands, both the rate of the nucleophilic coordination of the monomer and the probability of the fixation of the terminal unit in the *anti*-configuration as a result of the nucleophilic coordination of the penultimate unit increase, which leads to the 1,4-*cis*-structure of the polymer. The fact that in certain cases the influence of electron-donating ligands on the microstructure of polybutadiene, obtained in the presence of nickel-containing systems, resembles their influence in anionic systems is also striking in this respect: in both cases the content of 1,2-units increases. Thus it has been established[43–55] that the addition of triphenylphosphine to the nickel acetylacetonate + diethylaluminium chloride system with the ratios Ni : Al : P = 1 : 10 : 4 ensures the formation of polybutadiene containing 49% of the *cis*-units, 11% of the *trans*-units, and 40% of the 1,2-units.

However, one should note that this approach cannot explain all the features of the influence of ligands on the catalytic properties of the systems. In the $S_E Ci$ mechanisms, account is taken only of the influence of electronic factors from the standpoint of nucleophilic coordination and electrophilic insertion. Evidently, many oligomerisation reactions, proceeding via oxidation-reduction stages, cannot be treated, in principle, in terms of the $S_E Ci$ mechanisms. They include the majority of cyclic oligomerisation and co-oligomerisation reactions and certain linear oligomerisation reactions,[5] the key stages of which are oxidative addition (including those which lead to the formation of metallocycles) and reductive elimination. The catalysis mechanisms of these reactions constitute a special class and they are probably best referred to as redox mechanisms.

The steric effects of the ligands, which frequently play a decisive role in the overall catalytic action of the system, remain outside the range of phenomena which can be explained by the $S_E Ci$ mechanisms. These effects influence the mode of addition of the monomers, the process selectivity, the absolute rate constants for the elementary stages, and their ratios.

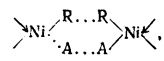
Ligands also have different effects on the number of catalytic centres. It has been established for the π-alkenylnickel chloride + quinone systems[41] that electron-accepting ligands diminish appreciably the concentration of such centres (4–10% of the concentration of the initial nickel compound). This conclusion was subsequently confirmed by a number of studies on the polymerisation of butadiene in the presence of catalytic systems based on π-alkenylnickel derivatives.[1]

It has been shown[42] that the interaction of π-alkenylnickel halides with electron acceptors (quinones) involves an oxidation-reduction polycomplex formation reaction leading to the formation of oligomeric and polymeric complexes with terminal alkenylmetal and metal hydride fragments containing electron-acceptor molecules bound in complexes. The formation of catalytic centres is accompanied by the formation of the products of the dimerisation of the alkenyl groups, which indicates the homolytic destabilisation of the Ni–C bond under the influence of electron-accepting ligands. The overall polycomplex formation scheme for the interaction of bis-π-crotylnickel chloride with chloranil is as follows:†



† Other possible reactions occurring in the polycomplex formation process have been considered by Azizov.[42]

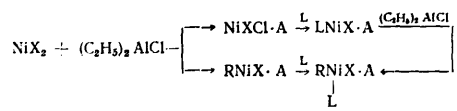
It has been suggested that the polycomplex grows via an intermediate cyclic state of the type



whose cleavage leads to the formation of the dimerisation products C_8H_{14} and the addition of a new unit to the growing end of the polycomplex. Mainly the terminal nickel atoms, constituting only a small fraction of the total number of nickel atoms, participate in the initiation of polymerisation. A low concentration of propagation centres obtains also in two-component systems of the Ziegler–Natta type, which has been established for the system based on organic dithio-derivatives of nickel and diethylaluminium chloride—10–40% of $[Na]_0$ depending on the reaction temperature.[37,40]

Electron-donating ligands exert opposite influences on the number of catalytic centres and the activation of the Ni–C bond. The increase of the effective propagation rate constant (αk_p) and the overall oligomerisation rate constant in the presence of a phosphorus-containing ligand, which is inconsistent with the increase of the activation energy for chain propagation, is striking.[24] This finding has been explained by the increase of the number of catalytic centres (or α) owing to their stabilisation as a result of complex formation with phosphorus-containing ligands. Such increase predominates over the decrease of k_p, which ultimately entails the growth of αk_p and of the overall rate of oligomerisation.

The conditions in the formation of the catalyst and the nature of the acido-ligand in the initial nickel compound also exert an appreciable influence on the number of catalytic centres in the system and hence on the effective codimerisation rate constant.[8] The preliminary formation of a three-component dithio-system in the presence of styrene entails a significant increase of the effective codimerisation rate constant.[8,28] On the other hand, the conditions governing the formation of the three-component acetylacetonate system do not exert an appreciable influence on this quantity. The activation energy depends little on the nature of the acido-ligand and on the catalyst formation conditions, but these factors do influence the pre-exponential factor, which reflects indirectly the changes in the concentration of the active centres in the system. Analysis of the changes in the pre-exponential factor in three-component systems, characterised by identical general kinetic features of the codimerisation reaction, permit the conclusion that the concentration of the active centres increases on passing from diethylphosphoro-dithioate to diethyl dithiocarbamate and when the catalyst is formed beforehand. The results of spectroscopic, cryoscopic, and kinetic measurements[8] have shown that this difference between the dithio-system and the acetylacetonate system is due to the slowness of the complex formation reaction between the dithio-derivative of nickel and the phosphorus-containing ligand, which takes place only after the interaction of the nickel compound with alkylaluminium halide:

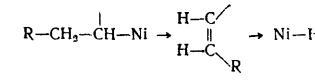


Thus, depending on the nature of the activating ligands, there is a possibility of both homolytic and heterolytic activation of the Ni–C bond in the catalytic centres. The former takes place under the influence of electron-accepting ligands, which is indicated, in particular, by the isolation of the products of the "quasi-radical" dimerisation of the alkenyl group in the reactions of π-alkenylnickel halides with electron-accepting compounds. The heterolytic activation of the Ni–C bond occurs under the influence of electron-donating ligands, which tends to decrease the activation energy for the insertion stage in the codimerisation of styrene with ethylene[8,28] and propene[29] and to increase the fraction of 1,2-units in the polymerisation of butadiene.[43–55]

The heterolytic activation of the metal–carbon bond is in certain cases apparently so great that the organometallic derivative of the transition metal becomes a catalyst of the anionic polymerisation of polar monomers, as happens, for example, in the polymerisation of methyl methacrylate in the presence of tris-π-allylchromium or the $Cr(acac)_3$–Al(isobutyl) system in combination with electron donors and also in the presence of complex catalytic systems based on vanadium and chromium compounds.[56] An analogous behaviour has been observed in the polymerisation of polar vinyl monomers under the influence of bipyridyl complexes of iron(II) and cobalt(I), having the d^6 and d^8 electronic configurations respectively.[57,58]

Homolytic activation is the main cause of the bimolecular destruction of active centres, occurring in the polymerisation of butadiene in the presence of the π-alkenyl halide + quinones[41] and nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride[40] catalytic system. However, overall, the stability of the catalytic action of the system depends not only on the nature of the activating ligand but also on the type of reaction catalysed. Thus the nickel *NN*-diethyldithiocarbamate + diethylaluminium chloride system, which propagates the polymerisation of butadiene in an unstable manner (the active centres are destroyed as a function of time[40]), proved to be entirely stable in styrene oligomerisation and codimerisation processes.[8,24,34] In our view, the stability of the action of the system is determined not so much by the thermodynamic stability as by the kinetic stability of the Ni–C bond in the intermediate organometallic centres, which is reflected in the frequency of the transitions: potential centre → actual centre and actual centre → potential centre. The hydride or organometallic derivatives of nickel are then regarded as the potential centres, while the actual centres are only its organometallic derivatives.

The intensity of these transitions depend on the ease of σ,π-isomerisation[59] in the intermediate organometallic derivatives of nickel. In principle, the isomerisation can proceed without a thermal effect or with only a small positive thermal effect. This is indicated by the comparison of the energies[2,60–62] and the bonds ruptured and newly formed in the reaction:



Bond	Ni–C	Ni–H	C–C	C=C	C–H	
Energy, kJ mol^{-1}	251	293	251	427	365	63–101

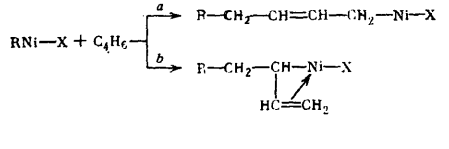
The intensity of the above transitions is therefore fairly high in the dimerisation, codimerisation, and oligomerisation processes in which intermediate alkylnickel derivatives are formed. There is insufficient time for the destruction of the catalytic centres via a bimolecular mechanism in any of the intermediate forms and the system proves to be stable. The transition: actual centre (growing chain) → potential centre (hydride or alkenyl derivative of nickel) in the polymerisation of butadiene is a slow reaction, which entails the possibility of a bimolecular destruction of the growing chains.

The intensity of the above transitions, which are in essence chain termination processes, determines also the molecular weight of the oligomerisation and polymerisation products. Among these transitions, hydrogen transfer, which proceeds with or without the elimination of a hydride complex from the

intermediate organometallic derivatives of nickel has special importance. The transfer with elimination occurs, as stated above, in dimerisation and codimerisation reactions and that without elimination takes place in oligomerisation and polymerisation processes. The ease of hydrogen transfer depends on the degree of σ,π hyperconjugation between the *d* orbitals of the metal atom and the σ bonding orbitals of the β-C–H bond.[2,63] Therefore all the factors leading to a decrease of the degree of σ,π conjugation (increase of the multiplicity of the bonding of the organic group to nickel in the sequence σ-alkyl < π-benzyl < π-alkenyl, the presence of bulky ligands in the coordination sphere of the metal, decrease of temperature, stereochemical factors) in the intermediate complexes can promote an increase of the molecular weight of the reaction products. The fact that the introduction of both electron-donating (tertiary phosphines, phosphites[24]) and electron-accepting (metal trichloroacetates[20-22]) ligands into the catalyst increases the molecular weight of oligostyrene, although it has different effects on the activation energy for the overall process, is important in this respect. Consequently, the molecular weight of the oligomerisation products depends primarily on the steric effects of the ligands and not on their electronic effects.

An analogous picture has been observed also in the polymerisation of butadiene; the less active π-alkenylnickel chloride + halogenoquinones systems ensure the formation of high-molecular-weight polybutadiene,[35,40,64] while the highly active catalysts based on organic dithio-derivatives of nickel lead to the formation of only low-molecular-weight products.[37,40] Analysis of the results of kinetic measurements[35,38] has shown that the former systems are sterically less favourable at the chain termination stage involving transfer to the monomer or the transfer of a β-hydrogen atom. In the latter systems, the transfer to the monomer is a hundred times and more faster (Table 3).

It is noteworthy that in the absence from the monomer of a β-hydrogen atom which can be readily split off, the polymerisation process in the presence of nickel systems can proceed via the mechanism of "living" chains. Thus the polymerisation of 1,1-dimethylallene in the presence of bis-π-allylnickel bromide takes place via this mechanism.[65] The "living" chains mechanism is observed also in the early stages of the 1,4-polymerisation of butadiene in the presence of π-alkenyl systems,[1,36,41,66] which has also been explained by the absence of a β-hydrogen atom capable of being readily split off from the growing alkenylnickel derivative formed on 1,4-dissociation of the double bonds of butadiene (pathway *a*):



It is therefore entirely possible that chain termination in the polymerisation of butadiene in the presence of nickel-containing systems via hydrogen transfer mechanisms takes place mainly as a result of 1,2-dissociation of the double bond (pathway *b*). The relation between the molecular weight and the microstructure of polybutadiene synthesised in the presence of *cis*-directing systems may serve, in our view, as important evidence in support of this hypothesis.[67] The relation is explained by the fact that the processes concerned with the regulation of both the molecular weight and the microstructure involve the formation of the same intermediate σ-complex (via pathway *b*), in which there is a possibility of interaction between the β-C–H bond and nickel.

The results of a study,[68] in which the possibility of the polymerisation of butadiene via the "living" chain mechanism up to high degrees of conversion of the monomer in the presence of the bis-π-allylnickel trifluoroacetate + triphenylphosphine or chloranil catalytic system has been established, constitute convincing confirmation of the above considerations. In the polymerisation in heptane at 55 °C (with the ratio P/Ni = 0.18), a linear relation is observed between the number-average molecular weight and the degree of conversion and a satisfactory correlation between the experimental and calculated degree of polymerisation. After the exhaustion of the first and the addition of new portions of the monomer, polymerisation continues and there is a further increase of $\bar{M}_n$. It must be specially emphasised that the content of 1,4-units in the polymer investigated reaches 99% and above and also the fact that the increase of the molecular weight is promoted by both electron-donating (triphenyl phosphite) and electron-accepting (chloranil) ligands.

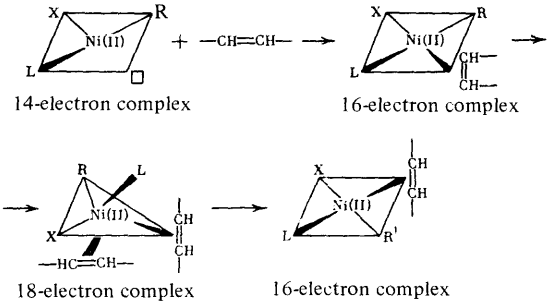
The conclusion that steric factors play a decisive role provides a key to the understanding of the principles governing the regulation of the structures and molecular weights of the products of the oligomerisation and polymerisation of unsaturated hydrocarbons in the presence of obtaining higher olefins and polyethylene from ethylene in the presence of these systems,[69-73] which had been previously thought to be unsuitable for these processes.

Steric effects influence also the selectivity of the codimerisation reactions of styrene with ethylene and propene. As shown above, on passing from a three-component to a two-component system, the selectivity of the codimerisation with respect to be ethylene (propene) which has reacted falls. Consequently, in the addition of the second monomer molecule to the active centres, steric hindrance in the coordination and insertion stages plays the main role and not the stabilisation energy of the newly formed Ni–C bond (which decreases in the sequence π-benzyl > σ-alkyl). In the presence of bulky phosphorus-containing ligands, the coordination of styrene is greatly hindered, as a result of which the ethylene (propene) molecule adds exclusively (or preferentially) to the intermediate benzyl derivative. In the absence of such ligands, the probability of the addition of the second styrene molecule increases and this lowers the selectivity of the codimerisation with respect to the styrene which has reacted.[8,24,27,29,30]

The opposite picture is observed in the addition of the first monomer molecule to hydride centres. As shown above, in the absence of phosphorus-containing ligands, the selectivity of the codimerisation with respect to the ethylene which has reacted, amounts to only 18%.[8,24] The remaining ethylene is converted into butenes, which means that ethylene and not styrene adds to a considerable proportion of the hydride centres. On the other hand, in the presence of phosphorus-containing ligands, styrene adds to them preferentially. The selectivity of the codimerisation with respect to the ethylene which has reacted then reaches 90–95%.[8,24] These results are also explained by the decrease of the probability of β-elimination from the benzyl derivative of nickel in the presence of phosphorus-containing ligands, hindering the σ,π-interaction, in the coordination sphere. Thus the steric effect of the ligands regulates not only the molecular weights but also the structures of the oligomerisation and polymerisation products.

However, one should note that, whereas the influence of electronic factors can be readily explained qualitatively from the standpoint of the S_Ei mechanism, this cannot be said of the steric factors. The latter apparently influence the geometry of the catalytic complexes, which in fact determines the very possibility of the catalytic process. In the

dimerisation and oligomerisation reactions catalysed by transition metal complexes, there may be transitions between 14-, 16-, and 18-electron complexes.[74,75] For nickel, the 18-electron complexes are less stable than the 16-electron complexes. Therefore, if the initial centre is a 16-electron organometallic or hydride complex, the coordination of the first monomer molecule can be completed by its insertion in the Ni–C or Ni–H bond. If, on the other hand, the coordination of one monomer molecule results merely in building up the coordination sphere of the metal with formation of a stable 16-electron square-planar complex, then insertion requires the coordination of a second monomer molecule. This results in the formation of a less stable pentacoordinate 18-electron nickel complex, which readily isomerises to the tetracoordinate 16-electron complex in the insertion process:

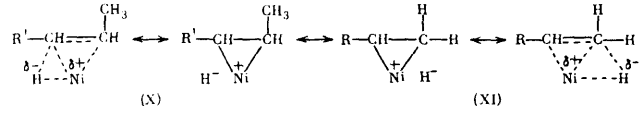


There is at present no information about the geometry of the active centres and it is therefore difficult to judge which of the geometrical dispositions is energetically most favourable. However, presumably the very possibility of the control of the sequence of the addition of monomers is determined primarily by the geometry of the intermediate states. The question of the monomer coordination and insertion sites is important in this respect. The few available experimental data show that, of the two mechanisms of the addition of olefins at the C–metal bond (*cis*-migration or insertion), *cis*-migration is preferred.[76] Evidently, in this case, for a specific disposition of the initial ligands, after each insertion stage three coordination sites appear alternately in the *cis*- and *trans*-positions relative to the ligand L. In relation to the organic group (or the α-carbon atom), the vacancy is always found to be in the *cis*-position.

The influence of the ligands on the selectivity of the codimerisation is probably determined by the different accessibilities of the *cis*- and *trans*-positions with respect to the ligand L in the coordination of monomers. In the codimerisation of styrene with ethylene (propene), ethylene (propene) is more readily coordinated in the *cis*-position in the intermediate benzyl derivative, while in the sterically less hindered *trans*-position in the initial hydride complex, the coordination of styrene is more favourable. The d_{π},π_{π} interaction between the non-bonding *d* orbitals of the metal and the π orbitals of the benzene ring is then facilitated, which yields an additional energy gain. In the case of the sterically less favourable derivative of L having *cis*-vacancies, the d_{π},π_{π} interaction is insignificant owing to the shielding of the non-bonding *d* orbitals of nickel by the bulky groups of the ligand L. Such alternation of the order in which the monomers are coordinated in combination with the *cis*-migration mechanism of insertion in the Ni–R bond ensures the exceptional selectivity of the codimerisation reaction.

Another version of the alternation mechanism has been proposed.[1,77,78] It has been suggested that the order in which the monomers are coordinated is determined by the number of vacancies in the coordination sphere of the metal. In the presence of a single free site, the olefin is more readily coordinated because it is more basic than the diene. In the presence of two vacancies, the coordination of the bidentate diene is more favourable. This mechanism explains satisfactorily the possibility of the formation of alternating copolymers of butadiene with α-olefins, but it can hardly operate in the codimerisation of olefins, each of which is capable of occupying only one coordination site. Apparently, depending on the nature of the metal, its ligand environment, and valence state as well as the geometry of the active complex, both versions of the alternation mechanism are possible.

Finally, one should point out that the mode of codimerisation is affected very strongly by the possibility of additional conjugation of any type. In the case of propene the greater probability of σ, π conjugation in the complex (X) compared with (XI) is apparently the main cause of the addition of nickel to the second carbon atom (contrary to the Markovnikov rule), which leads to the preferential formation of 4-phenylpent-2-ene:



In the presence of bulky ligands, the probability of σ,π conjugation diminishes, as a result of which there is in some cases an increase of the contribution by the addition of nickel to the first carbon atom and hence an increase of the content of the "tail-to-tail" adduct—2-methyl-3-phenylbut-1-ene.[27,29,30] The same effect probably occurs also in the dimerisation of propene, where the bulky phosphorus-containing ligands direct the process towards the formation of 2,3-dimethylbut-1-ene.[4–7]

Systematic studies[5,6] have shown that the influence of phosphines on the mode of addition of propene to the Ni–C and Ni–H bonds is determined to a large extent by steric factors, because among the *ortho*-, *meta*-, and *para*-substituted triphenylphosphines, an increase of the yield of 2,3-dimethylbut-1-ene and a decrease of the yield of hexenes are promoted solely by the *ortho*-substituted compounds. In the presence of aliphatic phosphines with similar electron-donating properties containing large organic groups, nickel forms a bond preferentially with the first carbon atom of propene in the first stage of the addition of propene to Ni–C, while in the absence of ligands it forms a bond preferentially with the second carbon atom [C(2)].

This has been explained by Henrici-Olivé and Olivé.[79] The authors suggest that, in the absence of steric hindrance by the ligand, the polarity of the double bond of propene is reversed in the coordination of the latter, as a result of which a negative charge appears on C(2). However, there are data according to which the addition of propene to the nickel hydride centres proceeds preferentially in the direction of Ni–C(2) even in the presence of phosphorus-containing ligands.[5,6] Consequently, the formation of the Ni–C(2) bond is presumably caused by the energy gain owing to the additional conjugation of the σ,π or $d_{\pi}p_{\pi}$ type and not by the reversal of the polarity of the double bond. On the other hand, if such interaction is blocked by the bulky groups of the ligand, then the addition takes place in accordance with the Markovnikov rule, i.e. in the direction Ni–C(1). Overall,

the addition takes place via the S_ECi mechanism when both carbon atoms in the coordinated olefin molecule carry a partial positive charge.

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