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Titanium compounds as catalysts for esterification and transesterification

M I Siling, T N Laricheva

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Abstract. Published data on the activity and selectivity of titanium-containing catalysts of esterification and transesterification reactions are surveyed. The influence of the nature of ligands and of the composition of the medium on the activity of catalysts is shown. The selectivity of the catalysis is considered from the viewpoint of information transmission theory. The bibliography includes 61 references.

I. Introduction

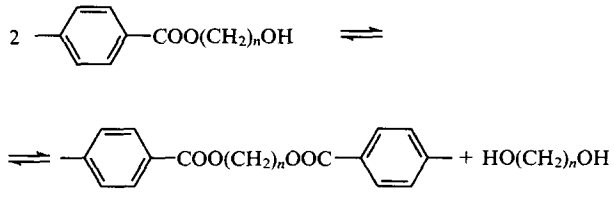
The esterification of carboxylic acids has been studied for 130 years. This reaction may be considered to be a classical topic of physical organic chemistry. Its investigation is associated with such names as Berthelot, Ostwald, Menshutkin, Guldberg, Waage, and others.[1] Esterification and transesterification reactions occupy an important place in industrial organic synthesis; they are widely used for the production of solvents, perfumes, polymers, and plasticisers.

Esterification reactions are traditionally catalysed by strong protic acids, which are active and cheap catalysts, although not free from certain drawbacks. Among these drawbacks one should note the low selectivity of protic acids caused by their ability to accelerate many side reactions, the necessity to neutralize the catalyst and to purify substantial amounts of effluent, and corrosion of the equipment.[2,3] This has stimulated the search for new catalysts for esterification and transesterification; a broad range of organic and inorganic compounds of various metals have been proposed as these catalysts, and titanium compounds occupy a special place among them. The high activity and selectivity of titanium-containing catalysts, their good solubility, and the absence of acidic effluent, which causes corrosion, are the reasons why these catalysts are frequently used in industry. Titanium compounds are used as catalysts for the synthesis of ester-based plasticisers, mostly dioctyl phthalate[3–5] and poly(alkylene terephthalates) — the polymers that have found application in the production of synthetic fibres, films, and structural materials.[5–8]

M I Siling, T N Laricheva Research Institute of Plastics, Perovskii proezd 35, 111024 Moscow, Russian Federation. Fax (7-095) 273 29 58

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In the present review, attention is concentrated on the titanium-containing catalysts used in the preparation of poly(alkylene terephthalates) (PATP) by the esterification of terephthalic acid with ethylene glycol, butane-1,4-diol, and other diols, by the transesterification of dimethyl terephthalate (DMT) with diols, and by the so-called polycondensation.



The latter reaction can also be regarded as transesterification in which one polymeric molecule acts as the ester and another one acts as the alcohol. It should be noted that the general rules of catalysis with titanium compounds manifested in these reactions are also valid for many other esterification and transesterification reactions.

Our review mostly deals with the activity and selectivity of titanium-containing catalysts. The problems of kinetics and mechanisms of the reactions are considered only in relation to the discussion of particular data on activity and selectivity. We also present nontraditional approaches to the mechanism of the catalytic action of titanium compounds based on the use of control and information theories.

II. The main groups of titanium-containing catalysts

It has not been our aim to consider the numerous patents in which the application of various titanium compounds as catalysts for esterification and transesterification is described. These data have been reported previously.[2–7,9] We shall restrict ourselves to the classification of the catalysts according to their chemical composition. In conformity with this principle, titanium-containing catalysts can be divided into organic, inorganic, mixed, and complex catalysts.

Compounds containing a Ti–OR bond (R is an organic radical) are usually referred to as organic catalysts. Among them, tetraalkyl titanates (alkyl orthotitanates or titanium alkoxides) $Ti(OR)_4$, where R = Et, Pr^i, Bu, are most frequently used. Some other titanium compounds have also been suggested as catalysts. For example, titanium salts of aromatic or aliphatic

carboxylic or dicarboxylic acids (formates, benzoates, oxalates), titanium polyacrylates and polymethacrylates, titanates of the general formula $Ti[O(CH_2CH_2O)_nH]_4$, where $n = 2, 3, 4$, obtained by the interaction of butyl orthotitanate with the corresponding diol, bis(chelate)bis(hydroxyalkoxy)titanates, and bis(chelate)bis-(oligoether)titanates, where the chelate is the residue of a chelating compound such as acetylacetone, dibenzoylmethane, 8-hydroxyquinoline, or ethyl salicylate. It has been shown that various oligotitanates, for example, compounds of the formula $RO[Ti(OR)_2O]_nR$, where $n = 2-20$, R = H, Et and/or Pr^i and/or Bu, can also be used.

Among inorganic titanium-containing catalysts, hexafluorotitanates $M_x(TiF_6)_y$, where M is an alkali metal, alkaline earth metal, zinc, antimony, or ammonium, are noteworthy. Data concerning the use of titanium oxides and hydroxides, orthotitanium acid and its salts have also been reported.

Organic compounds that incorporate, apart from oxygen (the Ti–O bond), atoms of other metals or other elements, such as halogens, Si, S, P, or N, belong to mixed titanium-containing catalysts. Metal hexaalkyl orthotitanates $MH[Ti(OR)_6]$ and $M'[Ti(OR)_6]$, where M is an alkali metal, M′ is an alkaline earth metal, and R is C_1-C_6 alkyl residue, are examples of this type of compounds. The use of titanium salts of aromatic thiols (thioxine, dimercaptobenzene, etc.) and compounds of the formula $M_x[TiO_2\cdot(C_2O_4)_2]_y$, where M is an alkali metal, alkaline earth metal, Sb, Sn, Zn, Pb, or Co has also been reported.

In recent years, complex catalytic systems consisting of several catalysts or containing one catalyst with functional additives have found wide application. This direction is very promising, since it appreciably widens the possibility of controlling the activity and selectivity of catalysts. Both organic and inorganic titanium compounds can serve as the main components of the complex catalysts for esterification and transesterification reactions. For example, catalytic systems based on tetraalkyl titanates and containing carboxylic acids, their salts, alkoxides of Group 3, 4, and 5 elements, organic compounds of sulfur, tin, bismuth, and antimony have been suggested.

Among inorganic titanium-containing catalysts with additives, mixtures of titanium metal with titanium hydrides and zinc acetate, mixtures of alkali and alkaline earth metal hexafluorotitanates with Li, Ca, Pb, Zn, and Mn salts of aliphatic carboxylic acids are noteworthy.

The above data illustrate the great diversity of titanium-containing catalysts for esterification and transesterification

III. The activity of titanium-containing catalysts

1. Comparison of the activities of titanium-containing and other catalysts

The higher catalytic activity of titanium compounds compared with similar compounds of other metals is manifested, for example, in the alcoholysis of alkyl benzoates.[10,11] Some of the results obtained are presented in Table 1.

As can be seen from Table 1, compounds of transition metals of the titanium and vanadium subgroups are the most active. The activation energy of the alcoholysis in the presence of Ti compounds (46.9 kJ mol^{-1}) is lower than that in the presence of other metal derivatives by a factor of almost two (84–105 kJ mol^{-1}).

Tetrabutyl titanate (TBT), as a catalyst of the reactions of heptanol with benzoic acid and methyl benzoate, i.e. esterification and transesterification reactions, is superior to Zn, Mn, and Co compounds.[12]

The catalytic activity of dibutyl tin dilaurate, dibutyltin diphenoxide, dibutyltin oxide, and tetraphenyltin in the transesterification of 4-hydroxybutyl benzoate at 167 °C, was two orders of magnitude lower than that of TBT,[13] the composition of organotin compounds having only slight influence on their catalytic activity.

Table 1. The activity of various catalysts in the alcoholysis of methyl benzoate with heptanol at 200 °C.[10]

Catalyst	Concentration of the catalyst (mol %)	Rate constant/ min^{-1}
$Ti(OBu)_4$	0.0190	1.0×10^{-2}
$Zr(Pr^iO)_4$	0.0200	3.0×10^{-3}
$Nb(OEt)_5$	0.0189	2.4×10^{-3}
$Ta(OEt)_5$	0.0203	5.7×10^{-3}
$B(OBu)_3$	0.0231	3.0×10^{-4}
$Al(Pr^iO)_3$	0.0193	2.0×10^{-4}
$Sb(OBu)_3$	0.0220	0.9×10^{-4}
$As(OBu)_3$	0.0203	0.8×10^{-4}

The influence of the nature of catalyst on the kinetics of the reaction of dimethyl terephthalate with butane-1,4-diol at a temperature of 175–225 °C and a catalyst content of 0.16 %–0.17% has been studied.[14] The rate of transesterification was monitored by following the liberation of methanol. In the series of catalysts $Co(OAc)_2$, $Mn(OAc)_2$, and $Ti(OPr^i)_4$, the latter exhibited the highest activity.

The kinetics of this reaction were studied at a DMT : butane-1,4-diol molar ratio of 1 : 2.2, a catalyst content of 5×10^{-4} moles per mole of DMT, and temperatures of 160–240 °C in the presence of zinc acetate, lead oxide, and TBT.[15] The highest degree of conversion, 98% after 4 h, was achieved with the titanium catalyst, while in the presence of PbO, it was 83% and with zinc acetate it was 75%.

It is known[7,16] that in the transesterification of DMT with ethylene glycol, titanium compounds exhibit lower catalytic activity than zinc, manganese, and cobalt acetates, which are usually employed in industrial processes.

The data presented imply that the activity of a catalyst in transesterification depends on the number of methylene units in the diol.

A number of papers have been devoted to the comparison of catalytic activities of various metal compounds in polycondensation in relation to the synthesis of poly(ethylene terephthalate) (PETP). Refler et al.[17] have studied the catalytic activity of metal butoxides in polycondensation in a thin layer of the polymer melt. At 280 °C and a catalyst content of 3×10^{-4} moles per mole of bis(hydroxyethyl) terephthalate, metals can be arranged in the following series in terms of their catalytic activities (rate constants, g $mmol^{-1}$ s^{-1}, and degrees of polymerisation are given in parentheses): Zn (2.5, 105) < Al (2.6, 99) < Ge (4.6, 114) ≪ Ti (6.4, 175) < Sn (7.9, 202). In the polycondensation of oligo(ethylene terephthalates), titanium derivatives are also more active catalysts than manganese or antimony compounds.

While analysing the data on the activity of catalysts for esterification and transesterification, one should take into account the fact that equilibrium constants of the reactions under consideration are low and are of the order of unity.[18] Therefore, the reverse reaction can substantially influence the rates of esterification and transesterification. In order to obtain data on the catalytic activity, independent of the reverse reaction, initial reaction rates should be measured or the process be conducted under conditions in which the reaction is virtually irreversible owing to the quick removal of the reaction products from the reaction zone. When esterification or transesterification reactions involve low-molecular-mass compounds, the realisation of these conditions is not difficult. A different situation occurs in the syntheses of polymers, especially when they are conducted in highly viscous media. For example, melt polycondensation of oligo(butylene terephthalate) used in the production of poly(butylene terephthalate) proceeds in a system in which the viscosity increases during the reaction to 5000–10000 Pa s.

The rate of the removal of the low-molecular-mass product, namely, butane-1,4-diol, from the reaction mixture in such systems may be low and comparable with the rate of the chemical transformation.

Thus, to compare the activities of polycondensation catalysts, one should take into account that the observed rate of the process may be determined not only by the rate of the chemical reaction, which is influenced by the catalyst, but also by the velocity of mass transfer. The latter depends on the thickness of the melt layer or on the interfacial area, which is a function of the intensity of stirring, composition of the reaction mixture, the temperature, and the degree of bubble-formation. Correct determination of the catalytic activity, based on the kinetics of polycondensation, requires that the above factors be taken into account in the mathematical model used for the calculations. The problems of mathematical modelling of the processes of the production of poly(alkylene terephthalates) have been considered by Adorova and Kuznetsov.[18]

In collaboration with Kuznetsov, we developed a procedure for studying the kinetics of polycondensation of oligo(alkylene terephthalates) convenient for the determination of the activity and the selectivity of a catalyst. In this case, the viscosity of the reaction medium is the most sensitive indication of the occurrence of polycondensation; it sharply increases in the course of the process. The change in the viscosity can be conveniently monitored by the increase in the power consumed in stirring the reaction melt. The power of an electric motor with mild [responsive] characteristics is directly related to the speed of the stirrer rotation, which can be easily measured. During the reaction the number of revolutions [per unit time] of the stirrer diminishes, the dependence of this value on the number-average degree of polymerisation of the product formed being nearly linear. It is notable that the rotation speed of a stirrer depends appreciably on the material of the reactor, in this particular case, on the kind of glass. This effect, which has been noted previously,[19] is probably due to the fact that the properties of the reactor material influence the adhesion of the polymer melt to the reactor walls and, hence, the processes of bubble and foam formation. These processes determine to a large degree the liquid-to-vapour interfacial area, through which the low-molecular-mass product of polycondensation is transferred. The effect observed indicates once again that mass transfer contributes significantly to the macrokinetic features of the polycondensation in the synthesis of poly(alkylene terephthalates).

The experimentally observed dependence of the number-average degree of polymerisation on the reaction time was treated using a mathematical model that took into account the following processes: (1) the formation of the ester bond via interaction of two terminal hydroxyalkoxycarbonyl groups or hydroxyalkoxycarbonyl and carboxyl groups; (2) side reactions yielding tetrahydrofuran and carboxyl groups (see below); and (3) the mass transfer of the diol and water liberated during the formation of the ester bond. The calculated rate constants for reactions (1) served as a measure of the activity of the catalysts studied, and the rate constants for reactions (2) served as a measure of their selectivity.

2. Catalytic activities of various titanium compounds. The effect of the medium

Several studies have been devoted to the influence of the nature of ligands (fragments) on the catalytic activity of titanium compounds. An evaluation of the activity of various titanium compounds in the esterification of 2-ethylhexyl hydrogen phthalate with an excess of 2-ethylhexanol at 170–175 °C and at a catalyst concentration of 0.01 mol kg^{-1} has shown that there is no substantial difference between the catalytic activities of the following compounds: titanium sulfate, titanium acetate, titanium dichlorodiacetate, titanium tetrachloride, TBT, tetra-2-ethylhexyl titanate, poly(butyl titanate), triethanolamine titanate, tributoxy titanium butyl hydrogen phthalate, and a complex of butyl levulinate with TBT.[20] Ortho- and metatitanic acids were found to be somewhat less active, and the catalytic action of titanium dioxide was much weaker. It is natural to attribute the low activities of the latter titanium-containing catalysts to their poor solubilities in the reaction medium.

Table 2. Catalytic activity of titanium compounds in the alcoholysis of methyl benzoate with heptanol at 200 °C.[10]

Catalyst	Concentration of catalyst (mol %)	Initial heptanol : methyl benzoate ratio/ mol mol^{-1}	Rate constant/ 10^{-2} min^{-1}
$Ti(C_7H_{15}O)_4$	0.020	21.50	0.96
$Ti(CF_3CH_2O)_4$	0.021	20.30	1.01
$Ti(C_2H_5OC_2H_4O)_4$	0.021	20.26	1.04
$Ti(C_4H_9O)_4$	0.020	20.17	0.83
$Ti(C_6H_5O)_4$	0.019	20.18	1.03
$Ti(Cl\text{-}C_6H_3Cl\text{-}O)_4$	0.019	19.47	1.06

The catalytic activities of various alkoxy and aryloxy titanium derivatives of the general formula $Ti(OR)_4$ in the transesterification of methyl benzoate with heptanol have been compared (Table 2).[10,21]

One can see that the nature of the organic radical does not influence significantly the reaction rate constant, which remains almost invariable even when twelve electronegative fluorine atoms or an aryl group are introduced into the catalyst molecule. Judging from the ability of alkoxy and aryloxy titanium derivatives to undergo quick radical exchange reactions, the results obtained were rationalised [10] in the following way: in the presence of excess heptanol, the alcohol and the catalyst undergo a quick exchange reaction giving tetraheptyl titanate. This was confirmed by NMR data. Therefore, alcoholysis reactions conducted in the presence of various titanium-containing compounds are characterised by nearly identical rate constants.

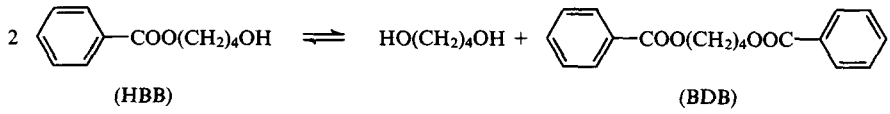
The formation of complexes and the radical exchange during the interaction of tetraalkyl titanates with esters and alcohols, as well as the formation of various complexes, have been reported.[22,23] It should be noted that in the general case, exchange reactions of the type

$$Ti(OR^1)_4 + nR^2OH \rightleftharpoons Ti(OR^1)_{4-n}(OR^2)_n + nR^1OH,$$

do not necessarily proceed up to the complete conversion of the initial tetraalkyl titanate to $Ti(OR^2)_4$. The position of the equilibrium is determined by the composition of the reaction mixture and by the equilibrium constant of the reaction. For example, in the TBT–*n*-heptanol system at 20 °C, the degree of conversion is 0.65, which corresponds to an equilibrium constant of 3.4.[23] In conformity with our data obtained by gas chromatography, in the transesterification of DMT with butanediol, 1.5–2 moles of butanol per mole of the catalyst (TBT) is liberated. These data imply that there is in principle the possibility of a substantial influence of the nature of the ligands in titanium-containing catalysts on their activities. Obviously, this effect should be most pronounced in the case of bulky and/or chelate-forming ligands, whose exchange may be hampered due to thermodynamic or kinetic restrictions. This is in agreement with published data.[24–26]

The catalytic activities of TBT and chelated titanium derivatives in the esterification of phthalic anhydride can differ by an order of magnitude.[25,26] Bis(acetylacetonato)dibutoxytitanium exhibited the highest esterification catalytic activity in a 2-ethylhexanol medium, and TBT was the most active when the process was carried out in di(2-ethylhexyl) phthalate.

In general, the rates of esterification and trans-esterification reactions, accelerated by titanium-containing catalysts, are appreciably influenced by the composition of the



(HBB) (BDB) (1)



(HBB) (BA) (2)

reaction medium.[12,26-28] This effect cannot be reduced to nonspecific solvation, which is measured in terms of the dielectric permeability of the medium. It is likely that the influence of the medium is mostly determined by the ability of titanium-containing catalysts to enter into various reactions with the components of the medium including the reagents.

For example, in a study of the esterification of 2-ethylhexyl hydrogen phthalate (monoester) to dioctyl phthalate (diester), it has been found[28] that in the medium of the monoester, TBT exhibits virtually no catalytic activity. In fact, in the beginning of the process, when the concentration of the monoester in the reaction medium is high and the concentration of the diester is low, an increase in the TBT concentration does not lead to any noticeable increase in reaction rate, which almost does not differ from the rate of esterification in the absence of the catalyst. As the reaction proceeds and the monoester content in the mixture decreases, the influence of TBT on the rate of the process increases appreciably. These data are supported by the results of Lemman et al.,[27,29] who found that when 2-ethylhexyl hydrogen phthalate or dioctyl phthalate instead of 2-ethylhexanol are used as solvents, the rate of the catalytic esterification of phthalic anhydride decreases in the following sequence: diester > 2-ethylhexanol > monoester. These experimental data were interpreted with a mathematical model, which made allowance for the reactions of TBT with the carboxyl group of the monoester, the hydroxyl group of the alcohol, and the ester group of the diester, that is, with all the main components of the reaction medium.[28] In addition, the effects of interaction between neighbouring ligands and the ligands of the inner and outer coordination spheres were taken into account.

3. The influence of additives and impurities on the catalytic activities of titanium-containing catalysts

The synthesis of PATP and other esterification and transesterification reactions are often carried out in the presence of titanium-containing catalysts mixed with other compounds. The question of how these additives influence the activity of titanium-containing catalysts is of interest both for the practice and for the theory of catalysis. Very little information concerning this problem has been published in the literature; therefore, the information provided by patent descriptions merits attention. An analysis of the latter has shown[9] that the use of complex titanium-containing catalytic systems may be favourable for both increase in the catalytic activity and improvement of the properties of the products obtained, for example, complex polyesters.

Ca, La, Zr, Co, Zn, Cd, Mg, Hg, Ge, Sn, and Sb derivatives, silver carboxylates, aromatic thiols, aliphatic and aromatic sulfonic acids, and their salts have been suggested as additives that increase the activity of titanium-containing catalysts.[9]

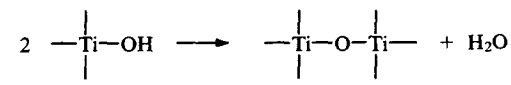
The problem of the influence of free carboxyl groups and water deserves particular attention, since they are virtually always present in the reaction mixtures. It should be noted that published data on this problem are somewhat contradictory. Despite the fact that carboxylic acids themselves are catalysts of alcoholysis, their influence on the activity of titanium-containing catalysts in esterification and transesterification is ambiguous. The addition of a small amount of adipic acid to TBT accelerates transesterification of its dimethyl ester with diethylene glycol.[30] The maximum rate constant was achieved at a concentration of COOH groups of 0.96 mol % with respect to dimethyl adipate. In some patents, carboxylic and dicarboxylic acids have been offered as activators for titanium-containing catalysts in the synthesis of PATP.[9] This made it possible to obtain polyesters with increased molecular weights.

However, a study of the synthesis of poly(butylene terephthalate) using model compounds in the presence of TBT at 150 and 167 °C has shown that benzoic acid deactivates the catalyst.[31] 4-Hydroxybutyl benzoate (HBB) was used as a model compound with a terminal hydroxyl group, benzoic acid (BA) was taken as a model compound with a terminal carboxyl group, and 1,4-butylene dibenzoate (BDB) was used as a model polymer. Attention was concentrated on the reactions modelling the polymer chain growth, namely, polycondensation (1) and direct esterification (2).

The results obtained in the experiments with various concentrations of the reactants and TBT led the authors to the following conclusions. Benzoic acid behaves as an inhibitor, if it is introduced in the reaction mixture together with TBT, or as a catalyst in the absence of TBT. In conformity with the coordination mechanism suggested for the catalytic reaction involving TBT, the inhibiting action of BA is caused by the formation of its adduct with the titanium-containing catalyst; this adduct is more stable than the adducts of titanium-containing catalysts with HBB or BDB. The existence of a stable Ti–BA adduct at room temperature in chloroform was confirmed by IR spectroscopy. However, the spectroscopic study provided no evidence supporting the existence of a product of addition of HBB to TBT under the experimental conditions. Based on the suggested mechanism, kinetic equations for calculating the rates of the formation of BDB and consumption of BA were derived. The calculated data proved to be close to the experimental results. It was also found that the stability of the BA–TBT adduct decreases appreciably with an increase in the temperature (the equilibrium constant for the adduct formation decreases by a factor of more than three as the temperature increases from 150 to 167 °C). Consequently, the inhibitory influence of BA is weaker at higher temperatures. The inhibitory effect of carboxyl groups on catalytic transesterification in the presence of titanium-containing catalysts is much less pronounced than that in the case of zinc-, manganese-, and cobalt-containing catalysts.[12]

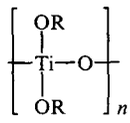
The influence of water on the activity of titanium-containing catalysts has not been fully elucidated. Many organic compounds of titanium are known[32] to be rapidly hydrolysed in the presence of even traces of water to give oligotitanates.





In a study of the kinetics of the transesterification of DMT with ethylene glycol,[33] it has been found that the activity of titanium-containing catalysts depends only slightly on the

added water. This is due to the low stability of aqueous complexes of titanium compounds, which are converted to polymeric derivatives of the following structure:



Ioda[33] managed to show experimentally that the catalytic activity of these compounds is nearly identical to that of the initial TBT.

An attempt has been made[34] to study the influence of the degree of preliminary hydrolysis of TBT on its catalytic activity in the esterification of phthalic anhydride with octanol. When the water : TBT molar ratio increased to 1.22 : 1 (which corresponded to a degree of TBT hydrolysis of 60%), the activity of the compound resulting from the hydrolysis became somewhat higher than the activity of the initial TBT. Further increase in the water : TBT molar ratio and in the degree of hydrolysis led to a monotonic diminution of the reaction rate, due to the decrease in the solubility of the TBT hydrolysis products. An analysis of the TBT hydrolysis products by IR and NMR spectroscopy and a comparison of their catalytic activities have shown that the products of TBT hydrolysis having a mainly linear structure are the most active. The increased catalytic activity of linear polytitanates is believed to be caused by the fact that they are more stable in the reaction medium than TBT, which incorporates reactive alkoxy groups.[34]

There are patents describing the use of oligotitanates as effective catalysts for the synthesis of PATP.[9] However, a study of the reversible reactions (1) and (2) has shown that water exerts an inhibiting influence on transesterification in the presence of TBT.[35] It was suggested that interaction of the catalyst with water and butane-1,4-diol affords catalytically inactive titanium derivatives. It was assumed that the active catalyst, water, and the inactive form of the titanium-containing catalyst exist in an equilibrium. Assuming that TBT is not capable of self-association under the reaction conditions and that most of the butoxy groups in its molecule have been substituted by alkoxy groups, Pilati et al.[35] has derived an equation for calculating the initial reaction rates at various initial ratios of the reactants. The results of these calculations are in good agreement with experimental data.

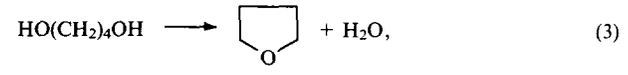
The above information indicates that the contradictory character of the data on the influence of carboxylic acids and water on the activity of titanium-containing catalysts is associated with the ability of the latter to enter into various reactions with these compounds.

IV. The selectivity of titanium-containing catalysts

The esterification and transesterification processes are accompanied, as a rule, by side reactions. First of all, there are various reactions of dehydration of alcohols and diols yielding ethers, including cyclic ones, aldehydes, and unsaturated compounds.[3-7] For example, usual products of the synthesis of PETP are diethylene glycol, 1,4-dioxane, formaldehyde, acetaldehyde, cyclic compounds, and some other compounds.[7] The major contributions are made by processes giving acetaldehyde and diethylene glycol and by the thermal degradation of the polymer.

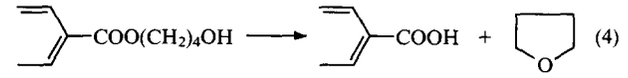
The major side products in the synthesis of poly(butylene terephthalate) are tetrahydrofuran, water, and acids. A TLC analysis of the products of the transesterification of DMT with 1,4-butanediol has shown that when titanium-containing catalysts or acetates of certain metals are used, no di(4-hydroxybutyl) ether is detected among the reaction products.[36] This was confirmed by NMR spectroscopy. Since THF is the main side product in the synthesis of poly(butylene terephthalate), the extent of its formation can serve as a measure of catalyst selectivity. Let us consider this problem in more detail.

Studies of a number of reactions involving model compounds and the real process[37-41] led to the conclusion that during the esterification of terephthalic acid or transesterification of DMT with butane-1,4-diol at 160–225 °C, THF can result from the dehydration of butane-1,4-diol



(3)

or from the cyclisation of the terminal hydroxybutylene groups.



(4)

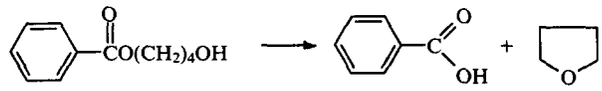
THF has also been detected by thin-layer chromatography among the products formed in the synthesis of poly(butylene terephthalate) without a catalyst.[42] In addition, as shown by IR spectroscopy, the polymeric product incorporates carboxyl groups. Based on these data, it was suggested that THF is produced via reaction (4). The same conclusion was drawn by Radias and Hall,[37] who have found THF in the products of polycondensation of bis-hydroxybutyl terephthalate in the presence of various titanium- or tin-containing catalysts.

In a kinetic study,[14] it has been shown that in the transesterification of DMT with butane-1,4-diol at a diol : DMT molar ratio > 2 in the presence of titanium isopropoxide at 175–225 °C, THF is formed mainly via reaction (3). The rate of the accumulation of THF varies only slightly with increase in the degree of the conversion of the monomers, because the number of terminal carboxyl groups, which catalyse dehydration of butane-1,4-diol, increases simultaneously with the decrease in the diol concentration. In the late stages of the polycondensation, the formation of THF from the terminal hydroxybutylene groups is likely to prevail.

It is logical to raise the question of the role of titanium-containing catalysts in the formation of THF via reactions (3) and (4). Analysis of the published data provides no unambiguous answer to the question whether or not titanium-containing catalysts accelerate the dehydration of butane-1,4-diol. It has been reported[37] that the heating of butane-1,4-diol at 210 °C for 8 h without a catalyst does not produce THF. According to another study,[38] butane-1,4-diol is dehydrated over a period of 4–5 h at 180–190 °C, THF being formed both without any added compounds and in the presence of TBT, benzoic acid, THF itself, or water. The reaction has a clear-cut induction period, which allowed it to be described as an autocatalytic reaction.[38] However, in our opinion, the attempt to attribute a catalytic influence to water or THF is dubious, especially in view of the fact that no substantial influence of added water or THF on the rate of dehydration of butane-1,4-diol was observed. The formation of THF on prolonged heating of butane-1,4-diol at 180 °C in the presence of various esterification and transesterification catalysts, including TBT, has been found by Moller et al.[43]

The general consensus of researchers on the influence of acidic additives is that acids are active catalysts of this reaction. For example, butane-1,4-diol is easily converted to THF on heating to 160–185 °C in the presence of orthophosphoric, benzoic, terephthalic, or hydrochloric acid.[9,37,38]

There are virtually no published data on the acceleration of reaction (4) by titanium-containing catalysts. Only Pilati et al.,[38] who have studied cyclisation of a model compound, namely, 4-hydroxybutyl benzoate, at 160–190 °C,



have shown that this reaction is not accelerated by acids and that catalysts used in the synthesis of PATP, including TBT, exert no influence on it.

The data presented indicate that there is no clear-cut catalytic influence of titanium-containing catalysts on the side reactions proceeding during the synthesis of poly(butylene terephthalate), which points to high selectivity of these catalysts. As regards their selectivity, titanium-containing catalysts of many esterification and transesterification reactions are superior not only to strong protic acids, but also to other metal-containing catalysts. This conclusion is in agreement with the results of a kinetic study [15] of the transesterification of DMT with butane-1,4-diol in the presence of various metal-containing catalysts in which TBT proved to be the most selective. A similar conclusion has been drawn by Suvaram et al.,[45] who have studied this reaction carried out at 220 °C and at a catalyst content of 0.1% by mass with respect to DMT. Titanium isopropoxide, phenoxide, diisopropoxyacetate, and triethanolaminate, calcium acetate, and antimony(III) oxide were used as the catalysts. It was found that in the presence of traditional catalysts for transesterification, for example calcium acetate, THF is formed in a high yield. Titanium-containing catalysts were much more selective, the best results being achieved with titanium isopropoxide. It has been shown [46] that the rate of the formation of a side product, namely diethylene glycol, during the synthesis of PETP in the presence of titanium-containing catalysts is lower than in the presence of antimony trioxide, which is frequently used as the catalyst.

In the patent literature, there is much information concerning highly selective catalysts for the synthesis of PATP based on titanium derivatives with added tin, antimony, germanium, lead, calcium, zinc, and manganese derivatives or amides of monocarboxylic acids, sulfonic acids, and phosphoric acid.[9] There are data concerning high selectivity of titanium-containing catalysts in other esterification and transesterification reactions. For example, TBT does not catalyse the side reaction of octanol dehydration during the esterification of phthalic anhydride with this alcohol.[47]

V. The activity and the selectivity of titanium-containing catalysts from the viewpoint of the theory of information transmission

The optimal catalyst should possess high activity and selectivity. The experimental data that refer mainly to enzymes, as well as to some chemical catalysts, indicate that it is possible to combine these characteristics in a single catalytic system. This possibility has been theoretically justified based on a cybernetic approach to catalysis developed in a number of studies.[8,9,48] The use of this approach made it possible to explain the remarkable activity and selectivity of titanium-containing catalysts for esterification and transesterification reactions.

According to the concept outlined by Siling,[8] a reaction system is regarded as being an object under control, a catalyst is considered to be a control device, and the rate of the reaction is taken to be a controlled parameter. The catalyst points to a reaction pathway that differs substantially from the noncatalytic one or, more precisely, it 'pilots' the reaction system along this pathway.

Any control is based on information transmission. In this case, one may speak of the information transmission from the catalyst to the reactants. The catalyst–reactant interactions serve here as the material basis for the information transmission. From the standpoint of statistical information theory,[8] the activity of a catalyst is largely determined by the diversity of these interactions.

To accomplish the main reaction, a catalyst should transmit particular information to the reactants. The information is transmitted along a communication channel as signals with the use of a certain code. In this particular case, the reaction system itself serves as the communication channel, a separate interaction of the catalyst with a reactant acts as a signal, and the space and time sequence of the interactions, which ensures the occurrence of the main reaction, is the code.

The information transmission along a communication channel is almost inevitably accompanied by errors (noise). This may be manifested, for example, as the omission of a necessary interaction, as the replacement of a necessary interaction by another one, or as the appearance of an 'excessive' interaction. Whereas the transmission of the nonperturbed information ensures the occurrence of the main reaction, the noise can be responsible for the side reactions. Thus, the problem of selectivity can be solved by using the theory of the information transmission along a channel with noise.[49] It should be noted that such a consideration will refer to the selectivity of the catalytic reaction, which does not always coincide with the selectivity of the overall process, first of all, due to the contribution of noncatalytic reactions.

The rate of the information transmission along channels with noise can be represented as jV, where V is the rate of the signal transmission, and j is the average information content of one signal. The latter value is a function of the probability of the appearance of errors in the signal transmission. The appearance of noise leads to the loss of information, and consequently j diminishes. As the probability of the appearance of errors decreases, j increases, and so does the rate of the information transmission. The highest possible rate of the information transmission for a particular channel with noise is referred to as the capacity of a communication channel.

If the amount of information transmitted in a unit time (I) is smaller than the channel capacity (C), then, in conformity with the Shannon theorem, there exists a way of presenting the information (coding), which makes it possible to transmit a message without delay and with a minor error. In the case where $I > C$, no way of coding that would provide high reliability and transmission of the message without delay can be chosen; however, as the coding becomes more perfect, the unreliability of the information transmission would decrease approaching the $I - C$ value, and the transmission rate would tend to C.

The Shannon theorem, as applied to catalysis, makes it possible to identify some general features concerning the reaction selectivity. First, it follows from the theorem that a selectivity as high as desired can in principle be achieved. It is known that this possibility is most fully realised in enzymic catalysis, though chemical catalysts that ensure the selective course of certain reactions also exist. One may believe that in these cases, the condition $I < C$ is met.

Regarding the relationship between activity and selectivity in a series of catalysts of the same type, one may assume from general considerations that the selectivity and the activity would vary, as a rule, in opposite directions, because transmission of a large amount of information is associated with a larger probability of an error. However, from the theorem it follows that this is not always true, and the relationship between activity and selectivity is determined by the manner in which the $I - C$ value varies over the given series of catalysts. In a series of catalysts for which $I < C$, there exists in principle the possibility of coding which ensures that high selectivity of the catalysts is retained as their activity increases. In a series of catalysts with $I > C$, limiting selectivity decreases as the $I - C$ difference increases. If, in this series, the channel capacity varies slightly and the activity grows with an increase in the amount of information transmitted, then selectivity and activity of the catalysts will vary in the opposing directions.

Thus, theoretical consideration indicates that different relationships between activity and selectivity in a series of single-type

catalysts are possible. This is consistent with experimental data (see, for example, the books by Golodets [50] and Gates et al.[51]).

In the context of information theory, the selectivity of a catalyst can be increased in the following ways.

(1) By increasing the capacity of the communication channel. With the average information content of one catalyst–reactant interaction being constant, the C value is determined by the number of the interactions in unit time. Therefore, high selectivity can be reached in those systems in which many fast interactions occur. Such situations are observed in enzymic catalysis,[52–54] which is one of the reasons why in this case the condition $I < C$ is satisfied. It is believed that it is the set of adsorption or other additional interactions of an enzyme with substrates that predetermines the high substrate specificity observed in the enzymic catalysis.

(2) By a decrease in the bulk of the information transmitted. The amount of information can be relatively small in the case where the reaction involves the cleavage and formation of a small number of bonds, and consequently, a great diversity of the catalyst–reactant interactions is not required. It has been noted [55] that one enzyme does not catalyse, as a rule, complex transformations involving cleavage and formation of many bonds. This requires a set of enzymes, each of them accelerating a relatively simple chemical transformation.

(3) By perfecting the coding procedure. According to information theory, correct transmission of messages along a channel with noise is favoured by connecting signals in long blocks. This way of coding is manifested in the catalysis as synchronous (concerted) reaction mechanisms, where the cleavage and the formation of bonds occur synchronously in a singe activation complex.[56–58] Mechanisms of this type are frequently realised in enzymic catalysis.

It can be seen that all the main factors contributing to the selectivity of catalysis from the viewpoint of information transmission are manifested in enzymic reactions. For our purposes, it is necessary to note the important role of the diversity of fast catalyst–reactant interactions, which ensures high channel capacity and effectiveness of coding.

Considering titanium-containing compounds in this context, one may suggest that the high activity and the high selectivity of these catalysts in esterification and transesterification reactions are caused by two main factors.

The first of them is the great diversity of the catalyst–reactant interactions. In fact, titanium is known to be capable of interacting with various oxygen-containing ligands.[32, 59, 60] Furthermore, tetraalkyl titanates tend to undergo exchange reactions at the Ti–O bond in which one oxygen-containing ligand is substituted by another. For example, in a tetraalkyl titanate–DMT–diol–oligo(alkylene terephthalate) system, a large number of coordination and exchange interactions occur leading to the appearance of the fifth and the sixth ligands at the titanium atom and to the complete or partial substitution of the OR groups by the molecules of the reactants and giving a wide range of mixed complexes and chelate-type derivatives. It is noteworthy that in the systems under consideration, information is transmitted not only via the interaction of titanium with the reactants or the components of the medium, but also via the formation of hydrogen bonds between these compounds and inner-sphere ligands (the interaction of ligands of the inner and outer coordination spheres and its role in catalysis have been considered in a number of studies.[8, 23, 28, 58, 61]). Of course, not all these interactions are stages of the catalytic process; moreover, some of them may retard the reaction (see for example, the paper by Siling et al.[28]). Nevertheless, it is the great diversity of the catalyst–reactant interactions that ensures the transmission of a large bulk of information from titanium-containing catalysts to the reactants. This diversity is a characteristic feature of complex catalytic systems based on titanium compounds.

High rates of the coordination and exchange reactions are the second factor. In fact, the high rate of exchange of alkoxyl radicals in the case of titanium alkoxides has been confirmed by NMR.[10, 22, 23] In terms of the rate of these reactions, metals can be arranged in the following sequence Ti > Sb > As.

The concept developed above is consistent with the fact that virtually all the titanium-containing catalysts suggested for esterification and transesterification are compounds with Ti–O bonds, which are prone to undergo a variety of fast reactions with the reactants, rather than compounds with Ti–C bonds.

As can be seen from the presented data, the application of information transmission theory to the problem of catalyst selectivity gives results consistent with the experimental data. In our opinion, the informational approach to catalysis has also a predictive ability. For example, one can speak of the design of an effective catalytic system, in which primary importance is assigned to the diversity and the rate of the interactions of the catalyst with the reactants. These interactions can be not only direct, but also indirect (with the participation of ligands of the outer coordination sphere).

* * *

This review covers studies published in the last 10–15 years and demonstrates the prospects of using complex catalytic systems based on titanium derivatives for esterification and transesterification reactions. Study of these catalysts may also prove to be fruitful in elucidating the general features of the homogeneous catalysis.

References

1. C K Ingold *Structure and Mechanism in Organic Chemistry* (Ithaca: Cornell University Press, 1969)
2. E G Maksimenko, V I Kirilovich, A I Kutsenko *Katalizatory Protsessa Proizvodstva Slozhnoefirnykh Plastifikatorov Polivinilkhlorida* (Catalysts of the Production of Ester Plasticisers of Polyvinyl Chloride) (Moscow: NIITEKhIM, 1981)
3. R S Barshtein, I A Sorokina, V G Gorbunova, in *Khimiya i Tekhnologiya Vysokomolekulyarnykh Soedinenii (Ser. Itogi Nauki i Tekhniki)* [Chemistry and Technology of High-Molecular-Weight Compounds (Advances in Science and Engineering Series)] (Moscow: Izd. VINITI, 1982) Vol. 17, p. 190
4. R S Barshtein, V I Kirilovich, Yu E Nosovskii *Plastifikatory dlya Polimerov* (Plasticisers for Polymers) (Moscow: Khimiya, 1982)
5. A Fradet, E Marechal *Adv. Polym. Sci.* **43** 51 (1982)
6. R S Barshtein, I A Sorokina *Kataliticheskaya Polikondensatsiya* (Catalytic Polycondensation) (Moscow: Khimiya, 1988)
7. B V Petukhov *Poliefirnye Volokna* (Polyester Fibres) (Moscow: Khimiya, 1976)
8. M I Siling *Polikondensatsiya. Fiziko-Khimicheskie Osnovy i Matematicheskoe Modelirovanie* (Polycondensation. Physicochemical Fundamentals and Mathematical Modelling) (Moscow: Khimiya, 1988)
9. T N Laricheva, I G Raskina, M I Siling *Katalizatory Sinteza Polialkilentereftalatov* [Catalysts of the Synthesis of Poly(alkylene terephthalates)] (Moscow: NIITEKhIM, 1989)
10. J Otton, S Ratton, V A Vasnev, G D Markova, K M Nametov, V I Bakhmutov, L I Komarova, S V Vinogradova, V V Korshak *J. Polym. Sci., Polym. Chem. Ed.* **26** 2199 (1988)
11. J Otton, S Ratton *J. Polym. Sci., Polym. Chem. Ed.* **26** 2183 (1988)
12. J Otton, S Ratton, V A Vasnev, G D Markova, K M Nametov, V I Bakhmutov, S V Vinogradova, V V Korshak *J. Polym. Sci., Polym. Chem. Ed.* **27** 3535 (1989)
13. F Pilati *Polym. Commun.* **25** 187 (1984)
14. L Yurramendi, M Barandiaran, J Asua *J. Macromol. Sci.-Chem., Part A* **24** 1357 (1987)
15. E Tucek, H Dinse *Acta Polymer* **31** 429 (1980)
16. K Wolf, B Kuster, H Herlinger *Angew. Makromol. Chem.* **68** 133 (1978)
17. G Rafler, F Tesch, D Kunath *Acta Polymer* **39** 315 (1988)

18. I V Adorova, V V Kuznetsov *Matematicheskoe Modelirovanie Protsessa Sinteza Polialkilentereftalatov* [Mathematical Modelling of the Synthesis of Poly(alkylene Terephthalates)] (Moscow: NIITEKhIM, 1987)
19. E Bonatz, G Rafler, G Reinisch *Faserforsch. Textiltech.* **24** 118, 309 (1973)
20. L M Bolotina, A I Kutsenko, E G Maksimenko *Plast. Massy* (7) 13 (1973)
21. G D Markova, K M Nametov, in *Polikondensatsionnye Protsessy i Polimery* (Polycondensation Processes and Polymers) (Nal'chik: Kabardino-Balkariya State University, 1986) p. 88
22. L I Komarova, N N Lapina, B V Lokshin, V I Bakhmutov, G D Markova, V A Vasnev *Izv. Akad. Nauk SSSR, Ser. Khim.* 1991 (1990)
23. L I Komarova, N N Lapina, B V Lokshin, V I Bakhmutov, G D Markova, V A Vasnev *Izv. Akad. Nauk SSSR, Ser. Khim.* 2001 (1991)
24. K Tomita *Kobunshi Ronbunshu* **33** 417 (1976)
25. E A Khrustaleva, M A Kochneva, L I Fridman, V G Lundina, A L Suvorov, A I Tarasov, V D Alekhina, L I Kurinkova *Plast. Massy* (10) 6 (1984)
26. E A Khrustaleva, Yu G Yatluk, A L Suvorov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1247 (1989)
27. V N Sapunov, G M Lemman, N N Lebedev *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Technol.* **19** 696 (1976)
28. M I Siling, V V Kuznetsov, Yu E Nosovskii, S A Osintseva, A N Kharrasova *Kinet. Katal.* **27** 98 (1986)
29. G M Lemman, Candidate Thesis in Chemical Sciences, Moscow Chemical Technology Institute, Moscow, 1974
30. Yu P Kudyukov, V Z Maslosh, I A Popova, E E Neskoredeva, T V Alekseeva *Plast. Massy* (12) 28 (1988)
31. F Pilati, P Manaresi, B Fortunato, A Munari, P Monari *Polymer* **24** 1479 (1983)
32. R Feld, P L Cowe *The Organic Chemistry of Titanium* (London: Butterworths, 1965)
33. K Ioda *Chem. Soc. Jpn., Ind. Chem. Seet.* **74** 1476 (1971)
34. S I Chervina, E G Maksimenko, R S Barshtein *Plast. Massy* (7) 31 (1987)
35. F Pilati, A Munari, P Manaresi, V Bonora *Polymer* **26** 1745 (1985)
36. T N Laricheva, I V Adorova, A Kh Bulai, M I Siling *Proizvodstvo i Pererabotka Plastmass i Sinteticheskikh Smol (Ekspress-Informatsiya)* [Production and Reprocessing, Plastics and Synthetic Resins (Express Information)] (5) 1 (1985)
37. A Radias, H Hall *J. Polym. Sci., Polym. Chem. Ed.* **19** 1021 (1981)
38. F Pilati, P Manaresi, B Fortunato, A Munari, V Passalacqua *Polymer* **22** 1566 (1981)
39. I V Adorova, A E Raver, T N Laricheva, in *Protsessy i Apparaty Proizvodstva Polimernykh Materialov, Metody i Oborudovanie dlya Pererabotki ikh v Izdeliya (Tez. Dokl. Vsesoyuz. Konf.)* (Abstracts of Reports of the All-Union Conference on Processes and Apparatus for Production of Polymer Materials, Methods and Equipment for Their Processing to Products) (Moscow: Moscow Institute of Chemical Machine Building, 1986) Vol. 2, p. 83
40. V Stah, E Poterasu, C Moisa, in *Abstracts of Reports of the Second National Congress on Chemistry, Bucharest, 1981* Vol. 1, Part 1, p. 64
41. M Tanaka, H Iida, H Ikeuchi *J. Soc. Fiber Sci. Technol.* **43** 35 (1987)
42. Yu Tong-yin, Fu Shon-kuan, Ch Chuan-yn, Ch Wei-zhung, Xu Rui-yun *Polymer* **27** 1111 (1986)
43. B Moller, J Blaesch, M Mudrick, G Rafler, H Zimmerman, H Stromeyer *Acta Polymer* **33** 38 (1982)
44. F Pilati, P Manaresi, B Fortunato, A Munari, V Passalacqua, in *IUPAC Macro Mainz [The 26th International Symposium on Macromolecules, 1979 (Short Communication Preprints)]* Vol. 1, p. 231
45. S Suvaram, V Upadhyay, K Phardway *Polym. Bull.* **5** 159 (1981)
46. T Yamada *J. Appl. Polym. Sci.* **37** 1821 (1989)
47. S I Chervina, E G Maksimenko, R S Barshtein, L M Vorob'eva *Kinet. Katal.* **32** 1157 (1991)
48. A Ya Malkin, M I Siling *Vysokomol. Soedin., Ser. A* **33** 2275 (1991)
49. V I Dmitriev *Prikladnaya Teoriya Informatsii* (Applied Information Theory) (Moscow: Vysshaya Shkola, 1989)
50. G I Golodets *Geterogenno-Kataliticheskie Reaktsii s Uchastiem Molekulyarnogo Kisloroda* (Heterogeneous Catalytic Reactions involving Molecular Oxygen) (Kiev: Naukova Dumka, 1977)
51. B C Gates, J R Katzer, G C A Schuit *Chemistry of Catalytic Processes* (New York: McGraw-Hill, 1979)
52. A D Klesov, I V Berezin *Fermentativnyi Kataliz* (Enzymatic Catalysis) Part 1 (Moscow: Izd. Mosk. Gos. Univ., 1980)
53. M L Bender, R J Bergeron, M Komiyama *The Bioorganic Chemistry of Enzymatic Catalysis* (New York: Wiley, 1984)
54. V K Antonov *Khimiya Proteoliza* (Chemistry of Proteolysis) (Moscow: Nauka, 1991)
55. L A Nikolaev *Osnovy Fizicheskoi Khimii Biologicheskikh Protsessov* (Fundamentals of the Physical Chemistry of Biological Processes) (Moscow: Vysshaya Shkola, 1976)
56. G K Boreskov *Zh. Vses. Khim. O-va im. D I Mendeleeva* **22** 495 (1977)
57. O M Poltorak, in *Kataliz. Fundamental'nye i Prikladnye Issledovaniya* (Catalysis. Fundamentals and Applied Investigations) (Moscow: Izd. Mosk. Gos. Univ., 1987) p. 7
58. K I Zamaraev *Usp. Khim.* **62** 1051 (1993)
59. I Shiihara, W T Schwartz Jr, H W Post *Chem. Rev.* **61** 1 (1961)
60. A A Grinberg *Vvedenie v Khimiyu Kompleksnykh Soedinenii* (Introduction to the Chemistry of Complex Compounds) (Leningrad: Khimiya, 1971)
61. V M Nekipelov, K I Zamaraev *Zh. Strukt. Khim.* **24** 133 (1983)