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Metalloporphyrins as Catalysts of Chain Transfer in Radical Polymerisation and Stereoselective Oxidation

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The results of studies on the catalysis of the chain transfer reactions in radical polymerisation and stereoselective olefin oxidation reactions in the presence of metalloporphyrins are surveyed. The problems of the synthesis of metalloporphyrins for catalytic studies are discussed.
The bibliography includes 43 references.

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I. INTRODUCTION

Studies of the catalytic properties of porphyrins and related macrocyclic compounds have developed vigorously in recent years. The interest in these compounds is due primarily to the fact that their metal complexes are involved in the most important processes in living nature—photosynthesis and the transport, fixation, and activation of oxygen.

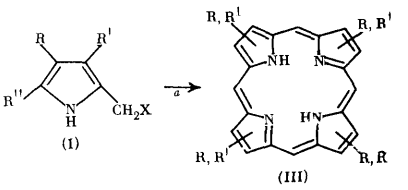
The principal results of studies, carried out under the overall supervision by N.S.Enikolopov, on the synthesis of porphyrins, the catalytic methods for the regulation of radical polymerisation with the aid of metal complexes, the synthesis and properties of immobilised catalysts, and the catalysis of stereoselective oxidation are summarised in this review.

II. THE SYNTHESIS OF PORPHYRINS FOR CATALYTIC STUDIES

The advances in physicochemical and biological researches into metalloporphyrins as well as the possibility of their practical employment as catalysts of various processes, dyes, medicinal preparations, etc. have been to a large extent determined by the level of synthetic developments in this field. Towards the beginning of the 1980's, extremely advanced methods were developed for the synthesis of asymmetric porphyrins based on the successive addition of pyrrole fragments with subsequent cyclisation, which made it possible to obtain compounds with virtually any specified structure. The achievements in this field of the porphyrin chemistry have been summarised in a review by Evstigneeva[1] and in a fundamental work edited by Dolphin[2]. However, compounds simplified to the maximum extent rather than complex multifunctional compounds are required for the purposes of the photochemistry, electrochemistry, analytical chemistry, kinetics, catalytic action, and the study of the reactivity of tetrapyrrole macrocycles. These compounds must contain a definite set of alkyl or aromatic substituents and must be readily soluble in water or organic solvents. The principal requirements which must be met in the synthesis of compounds to be used for practical purposes is ready availability of the starting materials and the existence of a technological procedure for the synthesis and purification of the required porphyrins.

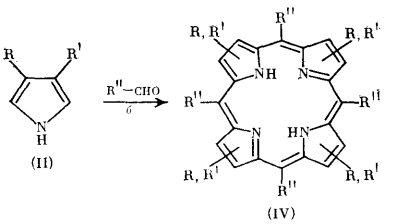
The development of studies in the field of the synthesis of porphyrins as potential catalysts proceeded via the preparation of derivatives with functional substituents, based on simple and ready available octa-alkylporphyrins and meso-tetra-arylporphyrins, and also via the improvement of technological schemes for the isolation and modification of porphyrins from readily available natural sources—haemin and chlorophyll.

Symmetrically substituted porphyrins are usually synthesised in a single stage via the cyclotetramerisation of 2,5-disubstituted pyrroles (pathway *a*) or via the condensation of 2,5-unsubstituted pyrroles in the presence of aldehydes (pathway *b*)[2]:



;

R, R' = Alk; R'' = H, COOH; X = OH, NH_2, $N(CH_3)_2$



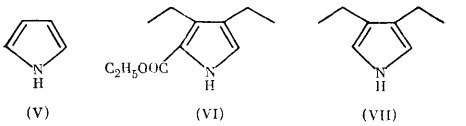
;

R, R' = H, Alk, R'' = Alk, Ar, 4(3)-pyridyl .

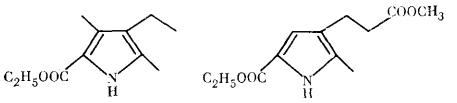
The exact positions of the groups R and R' in the porphyrins are not indicated in view of the formation of a racemic mixture of isomers when $R \neq R'$.

The synthesis of octa-alkylporphyrins (III) from the pyrroles (I, R, R' = Alk, R'' = COOH, X = OCH_3) is possible via pathway *a* with a yield of 70–80%. Pathway *b* leads to porphyrins (IV) in 70–80% yield when R, R' = Alk and R'' = H and 50–60% when R'' = Ar.

For practical requirements, it is possible to confine oneself to an extremely small number of initial pyrroles, whose employment makes it possible to solve the majority of problems in the synthesis of simple porphyrins. One such compound is the pyrrole (V), from which the preparation of *meso*-tetra-aryl(pyridyl, alkyl)porphyrins does not present special difficulties. The pyrroles (VI), (VII), and (VIII) are necessary for the synthesis of octaethylporphyrin and aetioporphyrin isomers—the most convenient models in a wide variety of physicochemical studies, while the pyrrole (IX) is used to model porphyrins with the natural structure.

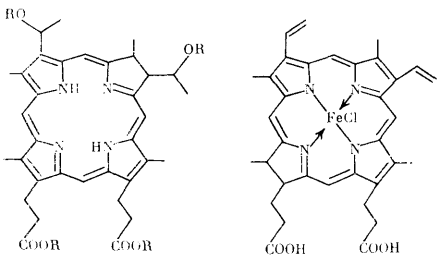


(V) (VI) (VII)

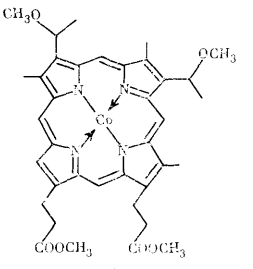


(VIII) (IX)

For an extensive investigation of the catalytic properties of porphyrins and related macrocycles, it was necessary to synthesise porphyrins and metalloporphyrins which would be highly soluble in organic non-polar or weakly polar solvents. For this purpose, an improved method was developed[3] whereby one could readily obtain the "tetra-alkyl ether-esters" (X) of haematoporphyrin, which consists in the successive treatment of the natural haemin (XI) with a solution of HBr in acetic acid accompanied by the addition of the corresponding alcohol to the reaction mixture.



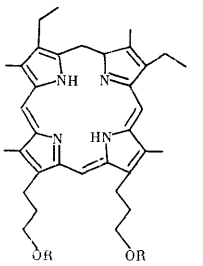
(X) (XI)



(XII)

The metal complexes of the "tetraether-esters", in particular the cobalt complex (XII), are readily soluble in the majority of hydrocarbons and other organic solvents, which made it possible to carry out extensive tests of the catalytic activity and to discover a new phenomenon in the radical polymerisation reactions—the catalytic chain transfer from the radical to the monomer[4].

However, the low stability of the metal complexes of the tetraether–esters significantly hindered their practical employment. A method was therefore developed for the synthesis of the more stable porphyrin (XIII) directly from haemin in yields up to 80%. The interaction of the porphyrin (VIII) with aliphatic acid chlorides, for example, with caprylic acid, makes it possible to obtain the corresponding esters soluble in any non-polar organic solvent and the reaction with acryloyl chloride yields the ester (XIV) which can be used for copolymerisation with methyl methacrylate and other acrylates in order to obtain porphyrin-containing polymers with catalytic activity.

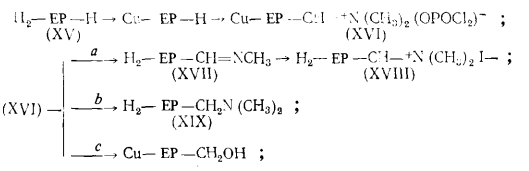


(XIII) R = H
(XIV) R = $COCH{=}CH_2$

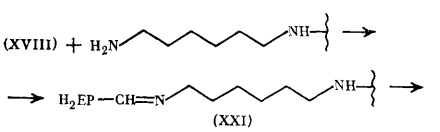
Another branch of studies in the synthesis of porphyrins in order to create catalytic systems involved the preparation of derivatives based on simple and readily available octa-alkylporphyrins and *meso*-tetra-arylporphyrins with functional group substituents.

The presence of a functional group as a substituent makes it possible to vary within wide limits the chemical properties of the porphyrin and also to graft metalloporphyrins to the surface of a solid carrier. Such immobilisation of porphyrin complexes makes it possible not only to create catalysts capable of being used repeatedly but also to increase greatly their concentration, preventing the precipitation from solution of sparingly soluble metal complexes. It has been shown that the use of the Vilsmeier reaction in relation to porphyrins leads to considerable possibilities for the synthesis of a wide variety of compounds containing a functional group substituent in both *meso*- and β-positions in the macroring. The optimum version of the Vilsmeier reaction is not the synthesis of the formylporphyrins themselves but the preliminary preparation of intermediate reactive "phosphate complexes", which are then used to prepare a wide variety of porphyrins with functional group substituents[5–10].

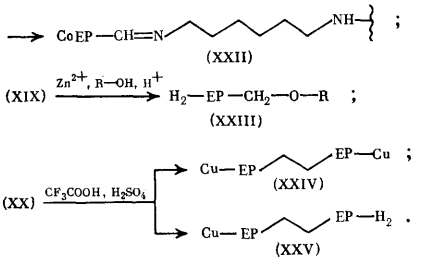
Examples of various reactions of one of the representatives of octa-alkylporphyrins, namely aetioporphyrin-1 (H_2-EP-H) (XV), which are of interest for the synthesis of catalysts, are presented below:



(XX)



(XXI)



Three main versions of the modification of the "phosphate complex" are possible. Pathway *a* permits the synthesis of a wide variety of Schiff bases under mild conditions and with a high yield. For example, the demetallation of compound (XVI) with concentrated H_2SO_4 and subsequent treatment with aqueous methylamine lead to the Schiff base (XVII), whose methiodide (XVIII) readily reacts with aliphatic amines to form Schiff bases in 85–95% yield. The interaction of compound (XVIII) with the "Separon" macroporous gel containing hexamethylenediamine residues leads to the immobilisation of the porphyrin on the surface of the carrier, as in the system (XXI). After the introduction of a cobalt ion into the porphyrin (XXI), a heterogeneous catalyst (XXII) was obtained and its properties were investigated comprehensively[8]. An analogous attachment of a porphyrin was achieved on glass beads and was completed by a finishing treatment with triethoxyaminopropylsilane.

Pathway *b* has not so far been tested in practice, but it is also of interest for the modification and immobilisation of metalloporphyrins. It has been found that the porphyrin (XIX), obtained from the complex (XVI) by reduction with $NaBH_4$ and demetallation in concentrated H_2SO_4, readily reacts with alcohols and CH acids (acetone, acetylacetone, nitromethane, and cyanoacetic or nitroacetic esters) to form the ethers (XXIII) and other compounds.

Finally, pathway *c* makes it possible to obtain the ethane-bisporphyrins (XXIV) and (XXV), containing one or two metal atoms in the molecule, from the complex (XX), formed in quantitative yield after the successive treatment of the complex (XVI) with aqueous alkali and $NaBH_4$. Similar compounds may be of interest in the study of the catalytic activation of simple molecules of the type of O_2, N_2, CO, and CO_2.

Thus, several reliable methods of synthesis of metal complexes of porphyrins, readily soluble in various organic media, are at present available to investigators. This creates extensive possibilities for the comprehensive study of the catalytic properties of such compounds in polymerisation, oxidation, dehydrogenation, and other reactions.

III. CATALYTIC REGULATION OF RADICAL POLYMERISATION

The vast majority of methods for the regulation of radical-chain polymerisation processes are based on the introduction of various inhibitors, moderators, and chain-transfer agents, reacting with the chain carrier radical in stoichiometric proportions close to unity[11]. Thus the regulation of the molecular weight (MW), for example, is achieved as a result of chain transfer reactions via a mechanism involving the abstraction by a macroradical $R_n^{\cdot}$ of individual atoms or fragments from the molecule of the chain transfer agent SX:

$$R_n^{\cdot} + SX \rightarrow R_nX + S^{\cdot} .$$

The radical $S^{\cdot}$ formed interacts with the monomer M and regenerates the kinetic chain:

$$S^{\cdot} + M \rightarrow SR_1^{\cdot} .$$

The mechanism of the action of polymerisation inhibitors can be analogous, the difference consisting in the fact that the inhibitor radical cannot regenerate the chain owing to its low reactivity.

New pathways leading to the regulation of the polymerisation process have been discovered—catalysis of the reaction involving chain transfer to the monomer (CCT) and catalysis of inhibition[12–19]. As a result of the discovery of CCT, it has been possible to regulate the MW of the polymers and catalytic inhibition made it possible to regulate the rate of polymerisation.

The CCT phenomenon has been observed in the presence of cobalt complexes of porphyrins (PCo). Catalytic inhibition is manifested in the presence of model porphyrins–cobalt-phthalocyanines (PcCo).

At the present time CCT has been thoroughly investigated in relation to the polymerisation of methyl methacrylate (MMA) initiated by azobisisobutyronitrile in the presence of the tetramethyl derivative of cobalt-haematoporphyrin[12–15]. Kinetic studies showed that CCT is a highly selective process, as a result of which the catalyst hardly influences the rate of polymerisation in the concentration range 10^{-6}–10^{-4} M, regulating the MW of the polymer in accordance with the familiar Mayo equation

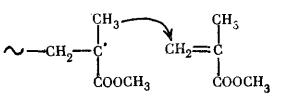
$$\frac{1}{\bar{P}_n} = \frac{1}{\bar{P}_{n0}} + C_n \frac{[M]}{[PCo]} ,$$

where $\bar{P}_n$ and $\bar{P}_{n0}$ are the average degrees of polymerisation in the presence and absence of the catalyst, $C_t = k_t/k_p$ is the chain transfer constant, k_t and k_p are the rate constants for chain transfer and propagation, and [M] and [PCo] are the concentrations of the monomer and the catalyst respectively.

The activity of the catalyst, estimated from the ratio of the chain transfer constants for the catalytic and non-catalytic reactions, is 10^8. The number of times each catalyst molecule is employed in the chain transfer steps reaches 10^5–10^6. Since the rate-limiting stage is the chain transfer to the metal complex and the regeneration process is fairly rapid, it was impossible to accumulate the intermediate in the catalytic reaction at concentrations sufficient for the investigation of its nature and reactivity.

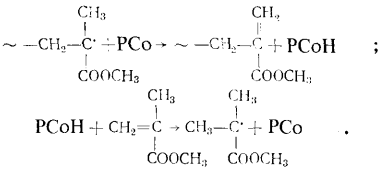
Information about the chain transfer mechanism was obtained with the aid of the NMR spectra of the oligomers[15]. Two alternative processes involving chain transfer to the monomer were analysed: via the transfer of a hydrogen atom from the radical to the monomer and via the transfer of a hydrogen atom from the monomer to the radical.

Analysis of the ratio of the intensities of the signals of the terminal and pre-terminal groups of the MMA oligomers, comparison of the average degrees of polymerisation determined from the NMR spectrum and by gel chromatography, and also analysis of the NMR spectra of the oligomers obtained from MMA deuteriated in the CH_3 group established that the chain transfer to the monomer takes place via the transfer of a hydrogen atom from the methyl group of the radical to the methylene group of the monomer:

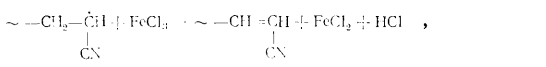


In order to explain the CCT phenomenon, the hypothesis was put forward that the active intermediate in the reaction is cobalt-porphyrin hydride. In order to demonstrate the hydride mechanism of the catalysis, the cobalt-porphyrin

hydride was synthesised[16] and in its presence MMA gave rise to an oligomer having the identical MW and structure to those of the oligomer obtained under CCT conditions. It has thus been established that the catalyst activates the polymeric radical during chain transfer and that CCT can be described by a scheme comprising concerted reactions involving the dehydrogenation of the radical and the hydrogenation of the monomer:



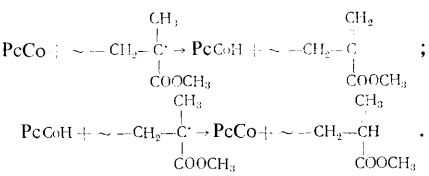
It had been known previously that the transition metal complexes interact with polymeric radicals via the oxidative abstraction mechanism[21], for example:



with rate constants in the range 10^5–10^6 litre mol^{-1} s^{-1}. Similar values of k_t, in the range (1–5) × 10^6 litre mol^{-1} s^{-1}, have been observed for cobalt-porphyrins[12]. However, one should note that only the presence of coordinated cobalt in a macroring with a specified structure constitutes the condition for the manifestation of CCT.

CCT has been observed also in the polymerisation of styrene and butyl acrylate[22,23], but in the former case its manifestation was complicated by the occurrence of side processes. In the polymerisation of butyl acrylate the rate-limiting stage is apparently the catalyst regeneration reaction and the process can therefore be regarded as reversible inhibition. One cannot rule out the possibility that the catalyst is regenerated via a mechanism involving the homolytic cleavage of the Co–C bond and not a mechanism with the dehydrogenation of the radical and subsequent transfer of the hydrogen to the monomer.

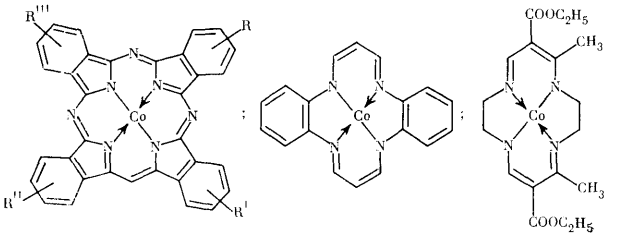
The study of the catalytic inhibition showed that the reaction proceeds via the following scheme:



The number of times each PcCo molecule is used in the course of a single polymerisation cycle is 10^2.

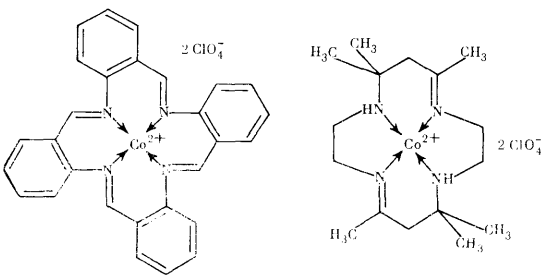
The CCT effect is manifested only when certain requirements are met by the structure of the catalyst molecule. The replacement of cobalt in the chain transfer catalyst by other metals, namely Cu, Fe, Ni, Zn, Rh, Mn, Pd, Mg, Pt, Sn, and U or by hydrogen leads to the complete loss of catalytic properties. Cobalt acetate, stearate, naphthenate, and acetylacetonate, cobalt-formazan, salcomin, and certain other cobalt complexes are inactive in the CCT to the monomer[19,23]. On the other hand, substituents in the macroring of the chain transfer catalyst do not play a decisive role in catalysis. When they are varied, the constant k_t changes within the limits of an order of magnitude[13].

It follows from the foregoing that the activity of the chain transfer catalyst is determined by the nature of the metal ion and the adjoining ligand environment and that the most important role is in this instance due to the π-electron system of the macroligand. The known chain transfer catalysts, namely the cobalt complexes of porphyrins, phthalocyanines (XXVI), tetra-azoporphyrins, and tetrabenzoporphyrins, hydroxycobalamin, and compound (XXVII), have an extensive π-conjugation system in the macroligand, which embraces almost its entire perimeter and which is quasi-aromatic in character.



(XXVI) (XXVII) (XXVIII)

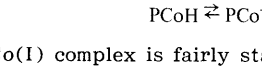
Cobalt complexes with a less extensive π-electron conjugation system along the perimeter of the macroligand, namely compounds (XXVIII) and (XXX), cobalt-formazan, etc., or a non-conjugated π-electron system, namely compound (XXIX), are incapable of catalysing chain transfer.



(XXIX) (XXX)

The observed characteristics of the molecular structure of the chain transfer catalyst made it possible to carry out a specific search for new promising catalysts and to discover them. Chain transfer catalysts with $k_t \cong 10^5$–10^8 litre mol^{-1} s^{-1}, readily available for extensive industrial application, have now been obtained. The rate of chain transfer in the presence of the catalyst is 10^{10} times greater than the rate of the non-catalytic reaction and CCT under the influence of metalloporphyrins is no less efficient than enzyme catalysis.

Although porphyrin complexes can contain cobalt(III), cobalt(II), or cobalt(I), only the cobalt(II)-containing forms are active, which is consistent with the hydride mechanism of the chain transfer catalysis. The Co–H bond in cobalt-porphyrins is polarised and the hydrides of the cobalt complexes behave as weak acids[25]:

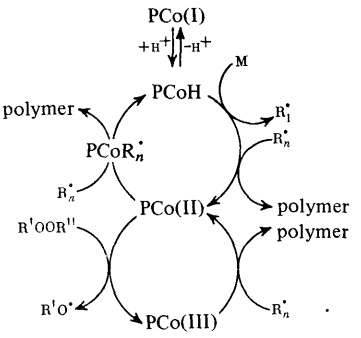


If the PCo(I) complex is fairly stable, for example, in the presence of amides, and the PCo(II) concentration in the polymerisation system is insignificant, then k_t is reduced by an order of magnitude. This is accompanied by a simultaneous increase of the rate of the catalytic chain termination reaction. Analogous effects have been observed in the presence of other porphyrin-like cobalt complexes.

Catalysts containing cobalt(III) are inactive in CCT, but under polymerisation conditions cobalt(III) is usually reduced to cobalt(II). The reduction reaction proceeds under the influence of chain propagation radicals via the oxidative chain termination mechanism[26,27] and is controlled by the axial ligand which determines the tervalent state of the cobalt atom. The addition to the polymerisation system of oxidants (benzoyl peroxide or cumenyl hydroperoxide), which selectively oxidise cobalt(II) to cobalt(III) in many catalysts,

leads to a decrease of the PCo(II) concentration and hence to a decrease of the rate of chain transfer.

The foregoing can be illustrated by the following scheme of the cyclic transformations of the catalysts in radical polymerisation:



One must note that the metal complexes investigated have many advantages compared with the familiar chain transfer agents. Thus, since the chain transfer constants in their presence are higher by 2–3 orders of magnitude than for the usual chain transfer agents, they can be introduced into the system at significantly lower concentrations in order to obtain polymers with a specified MW. The polymers thus obtained contain no fragments other than the monomer units, which is especially important in the synthesis of oligomers; on the other hand, the oligomers obtained, for example, by radical telomerisation, contain up to 15–20% of telogens, which impairs their operating properties.

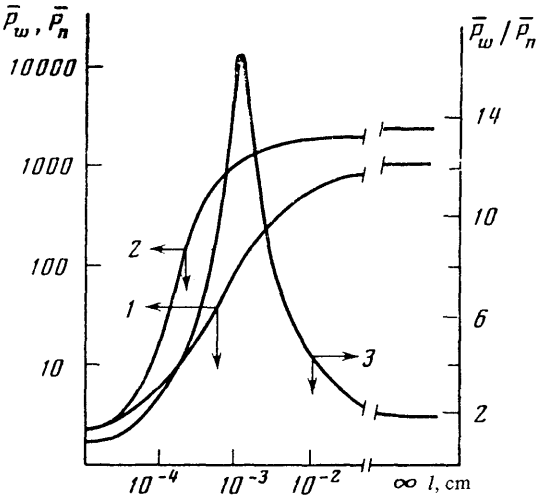
IV. KINETICS OF THE HETEROGENEOUS CATALYSIS OF CHAIN TRANSFER TO THE MONOMER

The idea of immobilising the chain transfer agent on the surface of an inert carrier in order to create catalysts capable of being regenerated was put forward immediately after the discovery of CCT.[18] Experimental and theoretical studies in recent years have now elucidated the fundamental possibilities and have led to the formulation of the main problems of heterogeneous catalysis using metalloporphyrins[8,28-30]. It has been shown that the catalytic properties of the metal complexes are not retained for all modes of addition to the surface. Thus the grafting of aetioporphyrin, attached in the *meso*-position by a single covalent bond to the "Separon" macroporous gel, leads to a catalytically active system after the introduction of cobalt. However, heterogeneous catalysts based on the *meso*-porphyrin-(II) and *meso*-porphyrin-(IX) dibasic acids have no catalytic activity. These catalysts were synthesised both by chemisorption on alumina and by grafting via amide bonds to the surface of porous glass treated with aminopropyltrichlorosilane[28].

It became evident that the covalent grafting of the metal complex onto the surface via a fairly flexible, long, and polar chain is necessary to ensure catalytic activity. This procedure was realised in the study of Pashchenko et al.[8] Subsequently the cobalt complex of tetraphenylporphyrin, which also possessed catalytic properties, was immobilised on the surface of "Separon" together with the cobalt complex of aetioporphyrin-(IX). The initial tests of the heterogeneous catalyst were carried out using the model MMA polymerisation reaction[14].

Since chain transfer in the presence of the heterogeneous catalyst takes place only on its surface, the problem arises of the role of the size of the unit cell, the reactant concentration, the viscosity of the medium, etc. in the regulation of the molecular weight distribution (MWD) in the product. The corresponding kinetic calculation of the rate of polymerisation and MWD was therefore carried out[29,30] for a model of the heterogeneous catalysis of chain transfer to the monomer. The process was modelled by the system of kinetic equations for radical polymerisation taking into account the diffusion of the reactants to the catalyst surface.

Calculations of the MWD and of the rate of polymerisation as a function of the reactant concentrations and the size and shape of the unit cell of the macroreactant explained both the common features and the fundamental kinetic differences between the CCT in the homogeneous and heterogeneous versions. In the former case the regulating factor is the volume concentration of the catalyst-chain transfer agent (PCo) and in the latter it is the linear size of the unit cell of the reactant (l).



An example of the calculated dependence of the MWD parameters and the polydispersity of the products on the linear size of the microreactor cell[44]: 1) $\bar{P}_n$; 2) $\bar{P}_w$; 3) $\bar{P}_w/\bar{P}_n$.

Whereas in the homogeneous version the polydispersity ($\bar{P}_w/\bar{P}_n$) of the product changes monotonically from 2 to 1 on increase of the catalyst concentration[17], in the heterogeneous version the polydispersity passes through a maximum as l diminishes (see Figure) and the fraction of the low-molecular-weight component of the MWD corresponding to polymerisation in a boundary layer increases. When the weight contributions of the low- and high-molecular-weight fractions are approximately the same, the maximum polydispersity of the product is observed.

In both homogeneous and heterogeneous catalysis of the chain transfer to the monomer, the overall rate of polymerisation becomes dependent on the efficiency of the transfer. The diffusion control of the disproportionation of the radicals leads to a decrease of the short chain termination constant, decreasing the rate of polymerisation.

A new geometrical factor, lowering the rate of polymerisation, appears in heterogeneous catalysis. It is the stationery gradient of the radical concentrations in the reaction cell.

The catalysis of chain transfer on the wall leads to a redistribution of the radical concentrations in space and the overall concentration of the active centres and hence the rate of polymerisation decrease at the same time. Numerical calculations for specific model variants on a computer confirmed this fully[30]. A 30% decrease of the rate of polymerisation in heterogeneous catalysis has been recorded experimentally[8], while the corresponding concentration of the cobalt complex of the porphyrin, dissolved in the monomer, did not lead to an appreciable decrease of the rate of polymerisation under analogous conditions. Experimental measurement of the rate of polymerisation in heterogeneous catalysis therefore not only constitutes a simple quantitative test of the efficiency of the catalytic properties of the surface but can also become a fundamentally new method for the investigation of the dependence of the elementary kinetic radical polymerisation constants on the length of the chain in macroradicals.

V. CATALYSIS OF OXIDATION AND HYDROXYLATION REACTIONS

It is known that metalloporphyrins catalyse the oxidation reactions of various organic and inorganic compounds. Oxygen is then coordinated to the central metal ion and one or two electrons are transferred to the oxygen with formation of superoxo- or peroxo-complexes which interact with the substrate and initiate its free-radical oxidation[31].

The processes involving superoxide complexes of porphyrins include the oxidation of adrenalin, which has been shown[32-34] to be catalysed by tetra-*p*-sulphophenylporphyrincobalt(PCo). It has been demonstrated that PCo forms a charge-transfer complex with oxygen which can dissociate to give a superoxide ion:

$$PCo + O_2 \rightleftarrows [PCo^{+}O_2^{\cdot-}] \rightleftarrows PCo + O_2^{\cdot}.$$

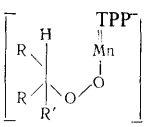
The interaction of $O_2^{\cdot}$ with adrenalin involves a complex mechanism and the first stable product is adrenochrome. The system described is highly effective in an aqueous medium at biologically important pH and each catalyst molecule participates in at least 100 oxidation steps.

The oxidation reactions initiated by superoxide proceed via a radical-chain mechanism with formation of a large set of products[32]. In the presence of an excess of the reductant, metalloporphyrins can catalyse also non-chain oxidation which is both regioselective and stereoselective. Thus the oxidation of olefins by molecular oxygen takes place extremely effectively in the presence of the manganese complex of *p*-methoxytetraphenylporphyrin (TPPMnCl) and an excess of sodium tetrahydroborate. This system models the action of mono-oxygenating enzymes, the haem prosthetic group of which incorporates metalloporphyrins in most cases. In living organisms monoxygenases catalyse the processes involving the incomplete incorporation of oxygen. One of the components of hydroxylase systems, cytochrome P-450, initiates the hydroxylation and epoxidation of steroid and aliphatic olefins, aliphatic acids, and alkanes. A characteristic feature of the action of hydroxylases is that the oxidation is by molecular oxygen and the presence of a reductant is necessary for the functioning of the system.

It is known that the porphyrin complexes of manganese(II), obtained by the reduction of manganese(III), activate molecular oxygen and catalyse the oxidation of various olefins[35-37]. This model hydroxylase system contains an excess of reductant, is insensitive to the action of radical inhibitors, and a set of products uncharacteristic of radical oxidation is formed in its presence. Saturated alcohols and ketones have been detected among the olefin oxidation products.

The oxidation of aliphatic (ethylene, propene, hex-1-ene, hex-2-ene) and steroid (androstene and cholesterol) olefins has been investigated at room temperature in dimethylformamide and a 1:1 benzene–ethanol mixture by molecular oxygen in the presence of the TPPMnCl–$NaBH_4$ system and it has been shown that mono- and di-substituted olefins are oxidised with formation of a mixture of ketones and alcohols[38,39]. Ketones and secondary alcohols are formed from asymmetrically substituted olefins (propene and hex-2-ene), i.e. the process is regioselective. The rate of oxidation of olefins depends on the substituent at the carbon atom involved in the double bond and varies in the sequence ethylene < propene < hex-1-ene < hex-2-ene. Tri-substituted steroid olefins are oxidised regioselectively and stereoselectively at a higher rate and with nearly 100% conversion, forming only 5α-substituted alcohols.

The formation of tertiary alcohols from trisubstituted olefins and of ketones and secondary alcohols from mono- and di-substituted olefins apparently proceeds via the same mechanism involving the reduction of TPPMnCl to a manganese(II) complex of TPP as the first stage with subsequent formation of a complex with molecular oxygen: TPP = Mn^{+}–O_2. In this complex manganese(II) and O_2 are located to one side of the plane of the porphyrin ring[40] and the electrophilic addition of the complex to the double bond of the olefin leads to the formation of a cyclic intermediate complex analogous to complexes involving monoxygenases[41]:



The reductive cleavage of the C–Mn bond by $NaBH_4$ leads to an intermediate product of the peroxide type, the mode of the subsequent cleavage of which depends on the structure of the substituents R and R' at the double bond. The formation of ternary metalloporphyrins–oxygen–olefin complexes has been observed experimentally[42]. Within the framework of the mechanism involving the formation of complexes of this type, it has been possible to formulate a kinetic scheme for the oxidation of olefins and to calculate the constants for the individual stages[43].

The effective charge of the metal ion and hence the degree of polarisation of the reactants in the formation of their complexes with the catalyst may be influenced by the presence of extraneous ions in solution. The introduction of neutral salts into the O_2 + TPPMnCl + $NaBH_4$ system inhibits the oxidation of cholesterol and the magnitude of the effect depends on the nature of the salt and the solvent.

As already mentioned, the catalytic system described above exhibits certain properties characteristic of monoxygenases: a non-radical character and hence the selectivity of the process catalysed, which proceeds via the formation of a cyclic intermediate complex, a high specificity of action, and inhibition by neutral salts. By altering the nature of the reducing agent, it is probably possible to change the direction of the process, obtaining, for example, epoxides as the primary

products, and, by altering the nature of the substrate, it is possible to achieve a higher affinity of the latter for the catalyst and hence a higher rate of oxidation.

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