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Catalysis and Coordination Interaction

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The following topics are reviewed: catalyst activity and co-ordination power; influence of co-ordination on ligand reactivity; influence of ligands on the catalytic activity of metal ions; co-ordination interaction and characteristics of the transition state of the catalytic reaction. Because interactions of the co-ordination type occur frequently in catalysis, the experimental results and the theoretical concepts of co-ordination chemistry can be fruitfully applied to problems in catalysis: various approaches of this type are discussed. The important role of mixed complexes and of dative interaction in the mechanism of many catalytic reactions is stressed. 210 references.

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I. INTRODUCTION

The mechanism of catalysis is determined primarily by the nature of the intermediate chemical interaction between the reagent (R) and the catalyst (C). The following are the two cases most frequently met: the R–C interaction is covalent in character, i.e. σ-electrons are directly involved; the R–C interaction is of the coordination type, i.e. with the direct participation of unshared electron pairs or of π-electrons in vacant orbitals. This subdivision is similar to the classification proposed by Roginskii[1], according to which catalytic processes can be divided into two large classes: oxidation–reduction and acid–base, i.e. with or without the fission of an electron pair (homolytic and heterolytic processes respectively).

The assignment of the R–C interaction to the covalent or the coordination type is fairly arbitrary. Often, and particularly in complicated reactions, interactions of both types occur simultaneously. Yet, each of these two types of interaction shows some characteristic features, and it is therefore convenient to discuss them separately.

The specific features of the coordination type interaction (CTI) are favourable to catalysis. Thus, a good catalyst should interact rapidly with the reagents, it should thereby influence their reactivity profoundly, and it should be easily regenerated. The electrons involved in CTI are the least firmly bound (n- or π-electrons), their energy levels lying above the level of the bonding σ-electrons. Hence, the activation energy of the complex-formation reaction is usually small, leading to fast interaction. Furthermore, coordination can have a marked effect on the reactivity of the ligand. Thus, it has been shown[2] that molecules bound to the catalyst surface by a hydrogen bond or by a stable covalent bond do not undergo alcohol dehydration and ethylene oxide polymerisation reactions. The most favourable bond energy in this case is that of molecules bound by coordination forces to a surface metal atom.

It does not follow, of course, that the R–C interaction is of the coordination type in all cases of catalysis. First of all, the participating molecules do not always have n- or π-electrons, and catalysts (e.g., metals) sometimes lack the requisite electron-acceptor properties. Furthermore, CTI does not always effectively weaken the "required" bonds in the reactant molecules (i.e., those which must be broken during the reaction). Thus, although alcohol and amine molecules can undergo CTI, the stability of the C–H bond is not appreciably affected. These compounds are usually dehydrogenated on metallic catalysts. In this case the R–C interaction which is responsible for catalysis is probably of the covalent rather than the coordination type. Thus, CTI can be the predominant type of interaction in those cases of catalysis where the electronic structure of both the reactant molecules and the catalyst is conducive to it (by weakening the bonds to be broken in the reaction or by assisting the formation of new bonds). Many heterolytic reactions belong to this type of chemical process.

Homolytic reactions also involve, on occasions, a significant amount of CTI, particularly when individual atoms or ions act as the catalytically active centre. However, the specific surface effect arising from the presence of free electrons in the solid catalyst, which is of fundamental importance in many cases of heterogeneous catalysis, is obviously not a case of CTI.

Because of the frequency with which CTI occurs in catalytic processes[3–12], there is a need to apply the experimental results and the theoretical ideas of coordination chemistry to problems in catalysis. The important advances in coordination chemistry made during the last two decades give reason to expect a deep penetration into the science of catalysis of the theories and ideas developed for complexes.

II. CATALYTIC ACTIVITY AND COMPLEX-FORMATION FUNCTION

The relationship between complex-formation and catalytic properties of a substance is determined by two basic factors: the tendency to undergo CTI with the reactants and the influence of this interaction on the reactivity of the species involved in the catalytic reaction. To illustrate this statement, we consider the simple catalytic reaction

$$R_1 + C \overset{K}{\rightleftharpoons} R_1C$$

$$R_1C + R_2 \overset{K}{\rightleftharpoons} R_1R_2 + C$$

where K is the equilibrium constant of the first step, and k is the rate constant of the second (rate-limiting) step. If $K \ll 1$ the observed rate constant is

$$k_{obs} = Kk.$$

In this equation K expresses the affinity of the catalyst for R_1, and k depends on the reactivity of this reagent in the intermediate complex. In general:

$$k_{obs} = f(K_1,...,K_n,k),$$

where K_1, ..., K_n are constants which characterise the equilibria preceding the limiting step. The expressions for k_{obs} are in keeping with the well known principle that the catalytic activity of a substance cannot in general be defined by thermodynamic quantities only. The properties of the reactants in the intermediate complexes must also be considered. We shall examine each of these factors separately in the following subsections.

1. Catalyst Activity and Coordination Power

Catalytic processes consisting of a single elementary step have a low probability. A multi-stage reaction implies some affinity between the catalyst and at least one of the reactants. Hence, and in view of the frequent occurrence of CTI in catalysis, we may conclude that the catalytic activity of a substance should be related to its ability to coordinate to the reactants. Correlations of this type have frequently been reported: one example is shown in Fig. 1.

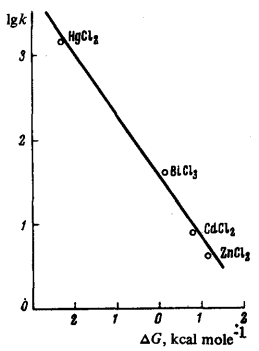


Figure 1. Catalytic activity of salts in the hydrochlorination of acetylene as a function of the stability of the catalyst–acetylene complex[46,47,167]: k is the rate constant for the reaction, ΔG is the free energy of formation of the $MCl_n.C_2H_2$ complex.

Information on the ability of the reactants to form complexes with various substances must obviously be of value in the selection of catalysts. The necessary data can be obtained, in the first place, from the accumulated fund of experimental material on the chemistry of complexes[13-19]. This approach to the problem of catalyst selection is subject to the following limitations: 1) existing data on the ability of reactants to form complexes with all the potentially useful catalysts are not sufficiently comprehensive; 2) the affinity of the catalyst for the reactant could be so low as to make an experimental study of the system excessively difficult; 3) the affinity could manifest itself only under conditions unfavourable to the study of complex formation.

The first of these limitations can be overcome to some extent by using published data on complex formation between the catalyst and some other compound, similar to the reactant in chemical structure. Strictly speaking, the molecules of the reactant and of the other compound should coordinate through the same functional group. The second and the third limitation should become less significant as more refined experimental techniques are developed. Lastly, all the limitations can be circumvented in principle by using theoretical ideas to evaluate the coordination power of a compound. Modern theories of the chemical bond in complexes (such as the valence bond theory, the crystal field and ligand field theories) allow useful though essentially qualitative predictions to be made of the possibility of coordination and of the stability of the coordinate bond. This problem has been discussed in a number of monographs and review articles[18-26,205]. Various semi-empirical relationships between the stability of the complex and characteristics of the central ion and of the ligand such as charge, ionisation potential, electronegativity, electron affinity, and polarisability can also be used[16,18,27-31].

Direct interaction between the catalyst and each of the reactants must, of course, be conducive to effective catalysis in multimolecular reactions, since it weakens the appropriate bonds of all the reacting molecules. Furthermore, the fixation of two or more reactant molecules close to an atom (or ion) of the catalyst can give rise to conditions which are sterically more favourable to interaction. In their discussion of the mechanism of enzyme action Braunshtein and coworkers[32] show that the formation of an intermediate complex (involving oriented contact of the reactants) produces a drastic increase in rate because low-probability, high-order reactions are replaced by first-order reactions. According to Bender[33], complex formation between the catalyst and both reactants can favour a bimolecular reaction by increasing the entropy of activation. Bender[33] and Eichorn[34] also point out that electrostatic repulsion should be minimised in the complex formed by a positively charged catalyst with nucleophilic reactants.

The above considerations justify the assumption that interaction between the catalyst and each of the reactants is involved in the mechanism of many catalytic reactions. In the case of CTI, mixed complexes may be formed. We shall consider a number of results which confirm the importance of mixed complexes in catalysis.

If the ability of the catalyst to coordinate to both reactants is important in many types of bimolecular catalystic reaction, compounds of metals able to form complexes with a wide variety of ligands should be the most effective catalysts. Grinberg[19] characterised the tendency of an element to form complexes in terms of the number of ligand types with which complexes are formed. In this sense, the Group VIII elements and the Cu, Zn, and Cr subgroup show the highest tendency to form complexes. These same elements, and their compounds, are found to catalyse many types of reaction.

There is experimental evidence that the mechanism of various enzyme processes involves the formation of mixed complexes between the enzyme and both reactants[35,36].

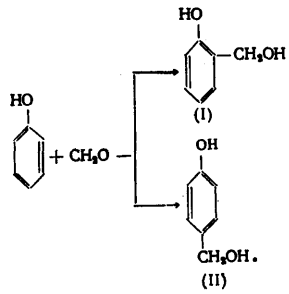
Flid and coworkers[37-43,53,54], and Gel'bshtein and coworkers[12,44-52], have studied in detail the addition of HX molecules to acetylene (where X = OH, Cl, CH_3COO). The reactions were catalysed by salts of metals of the Zn and Cu subgroups. It was found that these reactions involve, as an intermediate step, the formation and the transformation of a mixed complex (C_2H_2.catalyst.HX). The most convincing argument in favour of this mechanism is the experimentally established fact that the catalyst forms complexes both with C_2H_2 and with HX under the conditions of the reaction[12,43,45,46,51-54].

The retardation of various reactions by one of the reactants and the relationship between the coordination number of the metal atom or ion and its activity can be explained in the light of the role of mixed complexes in the mechanism of catalysis. Formation of the mixed complex is hindered when the catalyst shows too great a tendency to coordinate to one of the reactants, because all the free sites in the coordination sphere are occupied by one of the participants in the reaction. In this case the rate of the reaction can decrease as the concentration of this reactant increases. (This phenomenon, known as substrate retardation, is typical of many enzyme reactions[36].) A study of the kinetics of the vapour-phase synthesis of vinyl acetate from acetylene and acetic acid[48,51,55] has shown that the reaction is retarded by an excess of acetylene when catalysed by mercuric acetate, and by acetic acid when cadmium or zinc acetate are used as the catalyst. It has been suggested that the retardation arises from the formation of a complex between the catalytic salt and two molecules of one of the reactants, which prevents the formation of the mixed complex. This hypothesis was confirmed by adsorption measurements[12,50], according to which mercuric acetate can form a complex with two molecules of C_2H_2 under the conditions of the reaction, whereas zinc and cadmium acetates form complexes with two molecules of CH_3COOH. Order-of-magnitude agreement was obtained between the complex-formation constants of the catalytic salts with acetic acid calculated from the kinetic data by assuming the above mechanism[48,55] and the values determined from adsorption measurements[12,50].

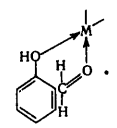
The smaller the number of free sites in the coordination sphere of a metal ion playing the part of the catalytically active centre, the lower will be its power to coordinate reactants, and in particular its power to form mixed complexes. This explains the known fact that the activity of an ion decreases, as a rule, as its coordination number increases. The effect is observed in a variety of catalytic reactions, for example in the decomposition of hydrogen peroxide catalysed by various catalase models[56], in the cracking and dehydration reactions of isopropanol on naturally occurring aluminosilicates[57], and in the solvolysis of fluorophosphates catalysed by various metal chelates[58].

The reactant molecules in the mixed complex take up well defined relative orientations: this effect can often lead to high catalytic specificity. According to Thompson and Busch[59], the coordination sphere of the metal ion can act as a matrix for the reaction, by imposing strictly defined positions on the reacting groups and thus controlling highly selective multistage reactions. The importance of the matrix function of the catalyst has been stressed by Roginskii[60].

The reaction between phenol and formaldehyde, giving saligenin (I) and *p*-hydroxybenzyl alcohol (II) as primary products, is a good illustration of the influence of mixed complex formation on the selectivity of the reaction:



When the reaction is catalysed by a proton acid (pH 1–2) the two phenolic alcohols are formed in approximately equal amounts[61,62]. On the other hand, catalysis by some metallic salts (such as zinc acetate) leads almost exclusively to the formation of saligenin[63,64]. This effect can be easily explained by postulating an intermediate mixed complex (III) whose spatial configuration favours reaction in the *ortho*-position:



(III)

The synthesis of phenolic alcohols belongs to the large group of heterolytic reactions which are accelerated both by proton acids and by aprotic (Lewis) acids. The observed differences in the catalytic action of the two types of acid can be ascribed to various causes, intimately related to the complex-formation properties of the catalyst. The proton is catalytically more active than aprotic acids in a number of reactions[9,58], but the opposite can also be true. Thus, the esters and amides of α-aminoacids are hydrolysed much more rapidly in the presence of Cu^{2+} ions than in the presence of hydrogen ions[65]. The catalytic activity of Hg^{2+}, Cd, Zn, and Bi chlorides supported on active carbon towards the hydrochlorination of acetylene in the vapour phase is much greater than that of HCl adsorbed on the carbon surface[47]. The liquid-phase hydration of acetylene proceeds quite rapidly in the presence of mercuric chloride, but it not catalysed to any extent by proton acids[37-40]. Many examples of this type could be quoted.

The very high activity of proton acids towards many reactions is evidently associated with the extremely small radius of the proton (10^{-13} cm), which is smaller than the typical radius of metal ions by 5 orders of magnitude. As a result, the proton is characterised by a high polarising effect as well as negligible steric hindrance.

The higher activity of aprotic catalysts in a number of cases is more difficult to explain. Many workers stress the greater positive charge of the metal ion[34,66], but this factor does not seem to be the essential one to the present writers. The electron-acceptor and the polarising power of a cation are determined by the parameters z/r and z/r^2, which involve the radius as well as the charge of the ion. It is obvious that the value of these parameters must be higher for the proton than for any metal ion, even

multiply charged. Furthermore, it now appears unlikely[67] that the metal ion in a catalyst structure carries a high positive charge.

Many workers[7,33,68,69] ascribe the high activity of Lewis acids (as compared with the proton) to the ability of a metal ion to coordinate to several reactants (or two groups in the molecule of a single reactant) at the same time. This view is consistent with the suggested importance of mixed complexes in catalysis.

Another possible explanation of the high catalytic activity of aprotic acids towards certain reactions should be mentioned. A large group of metal ions can exhibit electron-donating as well as electron-accepting properties in CTI, a function of which the proton is quite incapable. When activation of the reactant is mainly by dative C–R interaction we can expect metal cations liable to this type of interaction to show significantly higher catalytic activity than the proton. The acetylene addition reactions considered above are an example of this type of system.

2. Influence of Coordination on Ligand Reactivity†

In this section we shall discuss the influence of CTI between catalyst and reactant on the ability of the latter to undergo chemical change. Data on the reactivity of coordinated ligands should be relevant to this problem, whether an intermediate complex is formed during the catalytic reaction or whether CTI is confined to the transition state.

Coordination causes redistribution of the electron density in the ligand molecule, alters the interatomic distances and the bond angles, and therefore affects the polarity and the stability of the bonds. In general, therefore, coordination cannot fail to influence the reactivity of the ligand. Usually (but not invariably), the bonds nearest to the coordination bond are weakened. Coordination due to interaction between non-bonding electrons of the ligand and vacant orbitals of the metal atom shifts the electron density within the ligand molecule towards the central atom of the complex. As a result, the coordinated molecule becomes more electrophilic than the free ligand.

The situation becomes more complicated when dative interaction (leading to transfer of negative charge in the opposite sense, from the central atom towards the ligand) contributes significantly to the formation of the coordination bond. However, it does not follow that formation of a dative π-bond must weaken the influence of coordination on the reactivity of the ligand. When a double bond is formed between the metal and the ligand the disturbance caused by coordination extends over a greater number of electrons. Under these conditions the antibonding orbitals of the ligand become involved, and substantial weakening of some of the bonds within the coordinated molecule can ensue. Orgel[24] states that "the combined effect of two bond-formation mechanisms is much greater than the sum of the separate effects, because each mechanism removes the unfavourable charge accumulation due to the other".

The following are some of the most important sources of information on the reactivity of ligands in complexes: 1) data on the chemical reactions of coordinated molecules. (Unfortunately, very few data of this type are as yet available.) 2) infrared spectral data on the complexes. (The decrease in the force constant or the lowering of the stretching vibration frequency for a particular bond in the ligand molecule resulting from coordination can be taken as an approximate measure of the relative weakening of that bond.) 3) the effect of coordination on the E–H bond (where E = O, N, S, Cl, etc.) can be assessed by using relative data on the acid ionisation constant of the complex and of the free ligands. (The acid–base properties of complexes have been discussed in detail by Grinberg[19].) 4) indirect evidence on the influence of CTI on ligand reactivity can be obtained by comparing the catalytic activities of various substances in reactions involving the ligand in question.

We shall discuss the influence of coordination on the tendency of ligands to undergo chemical change by considering groups of ligands of a given type. This approach should be fruitful because it allows us to apply existing data to the problems of catalysis, and in particular to catalyst selection and the mechanism of catalysis.

Amines

Amines coordinated through the lone pair of electrons on the nitrogen atom show a weakening of the N–H bond, which manifests itself in an enhancement of the acidic properties of coordinated amines[19]. For example, the ionisation constants of complexes with imidazole derivatives are higher than those of the free ligands by 3–4 orders of magnitude[70–72]. The large drop in the N–H stretching vibration frequency observed[73–77] in the infrared spectra of the complexes (as compared with the uncoordinated amines) is consistent with these results. In complexes with different metals this frequency decreases as the stability of the complex increases. Thus, a study of the infrared spectra of aminoacid complexes with various bivalent metals[77] has shown that ν_{N-H} for the complexes is consistently lower than for the sodium salts of the aminoacids. The authors ascribe this frequency shift to an increased positive charge on the nitrogen on formation of the M–N bond, resulting in a decrease of the N–H force constant in proportion to the strength of the M–N bond, i.e. to the stability of the complex. According to Filimonov and Bystrov[76], the strength of the N–H bond in the coordinated amine is influenced not only by the lower electron density on the nitrogen atom, but also by the change in hybridisation of the nitrogen valency orbitals resulting from coordination. It has been pointed out[74,75] that hydrogen bond formation between a coordinated amine and an anion in the outer sphere of the complex can also weaken the N–H bond and shift its absorption band towards lower frequencies.

Several workers have studied the reactions of ammines. Chugaev[78] showed that HCl is eliminated from chloropentammineplatinum(IV) chloride under the influence of alkali:

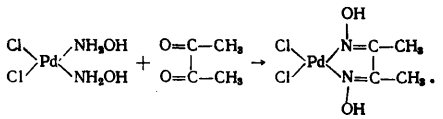
$$[Pt(NH_3)_5Cl]Cl_3 + NaOH \rightarrow [Pt(NH_3)_4NH_2Cl]Cl_2 + NaCl + H_2O.$$

Grinberg and Gil'dengershel' found[79] that ethylamine molecules in the inner sphere of a Pt^{4+} complex can be hydrolysed to ethanol and ammonia, the latter remaining coordinated to the platinum. Very drastic conditions are needed to hydrolyse free aliphatic amines, and hence we may conclude that coordination weakens not only the nitrogen–hydrogen but also the nitrogen–alkyl bond. Kukushkin[80–84] has made a detailed study of the chlorination of ammonia bound in various Pt^{4+} complexes, and found that the rate constant for coordinated ammonia can be higher or

†For a review of the early work, mainly up to 1940, the reader is referred to Ref. 3.

lower than for the ammonium ion, depending on the charge of the complex ion and on the nature of the ligands.

It has been reported[85] that coordinated hydroxylamine can be condensed with α-diketones with formation of dioximes;



Activation of the N–H bond as a result of CTI should evidently be noticeable in the catalysis of specific amine reactions by Lewis acids. Reactions of this type include the interaction of amines with ketones (catalysed by Zn and Cd salts[4]), the synthesis of mono-, di-, and trimethylamines from ammonia and methanol over alumina, the synthesis of flavanthrone by condensation of 2-aminoanthraquinone in the presence of $SbCl_3$, used in the production of dyestuffs, etc.

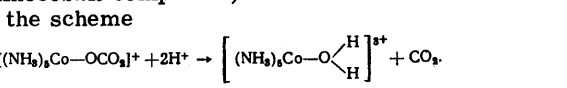
Oxygen-containing ligands. The coordination of ligands through an oxygen atom usually weakens the bonds adjacent to M–O. It is well known that complex formation increases the acidity of oxygen-containing molecules[19,86-88]: for example, the acidic ionisation constant of the aquo-ions of various metals is several orders of magnitude higher than the value for water. This is consistent with the observation[74] that the stretching vibration frequency of water is drastically decreased by coordination.

The spectra of the complexes of ligands containing carbonyl groups, such as ketones, esters, salicylaldehyde, tropolone, etc., have been studied intensively[73-75]. As a rule, coordination lowers the frequency of the C=O stretching vibration, obviously because the multiplicity of the bond is lowered by the shift of the π-electron cloud towards the oxygen atom[74]. The parallelism between this lowering of frequency and the stability of the complex has been repeatedly stressed.

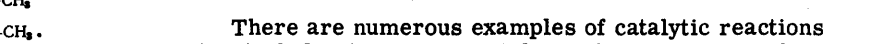
Nakamoto's analysis[75], of the infrared spectra of metal acetylacetonates leads to the conclusion that coordination of acetylacetone causes a weakening of the C–C as well as the C–O bond. It has been stated[73-75] that coordination of the carboxylate anion $(R-C\overset{O}{\underset{O}{<}})^-$ produces a lowering of the stretching vibration frequency for one of the C–O bonds, whilst at the same time increasing the frequency for the other C–O bond. Thus, the coordinated carboxyl group approximates to the structure $-C\overset{O}{\underset{O^-}{<}}$, characteristic of esters.

The weakening of the bonds adjacent to the coordination bond produced by complex formation is made evident by the reactions of oxygen-containing ligands. Meerwein and Hinz[89] had found, as long ago as in 1930, that butyl methyl ether is formed when diazomethane is passed through solutions of some salts ($ZnCl_2$, $FeCl_3$, etc.) in butanol. Free butanol does not undergo this reaction. Meerwein therefore suggested that dissolution of these salts in the alcohol involves the formation of complexes of the $\begin{matrix}R\\H\end{matrix}\!\!>\!O\ldots MX_n$ type.

Hunt and coworkers[90] showed, using ^{18}O, that the Co–O bond is not broken during acid hydrolysis of carbonatopentaamminecobalt complexes, and that the reaction occurs by the scheme



Phenyl esters complexed with $AlBr_3$ split off alkyl bromide when heated in benzene, and are subsequently hydrolysed to phenol by water[91]. Benzoate esters complexed with Hf or Fe chlorides undergo thermal decomposition with evolution of alkyl chloride[92,93]. For example,

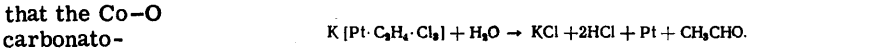


There are numerous examples of catalytic reactions in which CTI between a metal ion of the catalyst and an oxygen atom of the reactant plays a mechanistically important role. There is little doubt that the weakening effect of this interaction on the O=C, O–C, O–H bonds and also on their neighbouring bonds is one of the key factors in many catalytic reactions. Typical of these are the decarboxylation of keto-acids, catalysed by various metal ions[94,95], the dehydration of acids and alcohols[2,96] over Al_2O_3, the Friedel–Crafts alkylation and acylation of aromatic compounds, the synthesis of phenol–formaldehyde resins of the *ortho*-Novolak type[63,64,97], the hydrochlorination of methanol on metal chlorides[98] (Cd, Zn, and Bi), and others.

Alkenes and alkynes. A considerable amount of work has been done on the coordination of olefins and acetylenes, and several review articles have been published[99-104]. Dewar[105,106] has suggested that coordination of unsaturated compounds involves the interaction of π-electrons from the ligand with vacant orbitals of the metal ion, as well as dative interaction between *d*-electrons from the metal and antibonding π-orbitals of the ligand. Experimental confirmation of Dewar's views has recently been obtained (see Ref. 104), and these views are now generally accepted. Thus, the metal ion in general shows both acceptor and donor properties in the coordination of unsaturated ligands. Because of the acceptor and donor behaviour of the central ion of the complex, the electron population of the bonding π-orbitals of the ligand decreases, and the population of the antibonding orbitals increases. Hence, the coordination of unsaturated compounds at a carbon–carbon multiple bond should cause weakening of this bond. Many workers have in fact reported a significant lowering of the stretching vibration frequency of a multiple bond as a result of complex formation: for example, in studies of the Ag^+ complexes with alkenes and alkynes[107,108], of compounds of the Zeisse's salt type[109-111], of the acetylene complexes of copper and platinum[112,113], and others (see Refs. 73–75).

In some systems, coordination also weakens the =C–H and ≡C–H bonds. The acidic properties of acetylene and vinylacetylene are enhanced by complex formation with Cu(I) salts[114,115]. Temkin[43] made an analysis of the published data on the excited states of acetylene, and concluded that dative interaction has a profound effect on the weakening of the C–H and C≡C bonds.

The activation of olefins on coordination is reflected in the reactions of many platinum complexes[103]. Thus, bromine reacts with olefin complexes to form bromosubstituted olefins. The ethylene complex is rapidly and quantitatively reduced by hydrogen at room temperature with formation of ethane. Zeises's salt is decomposed by hot water according to the equation



A similar reaction occurs also with the ethylene complexes of platinum[116,129].

CTI plays an important part in determining the mechanism of the catalytic reactions of alkenes and alkynes. We

need mention only the reactions of olefin polymerisation[117-126], oxidation of ethylene to acetaldehyde[127-134], and acetylene addition reactions[37-55]. Many workers[12,40-43,47-52,135] have stressed the importance of dative interaction in the catalysis of the reactions of unsaturated compounds.

Aromatic compounds. Coordination interaction between aromatic hydrocarbons and metal cations can arise through the π-electron system of the hydrocarbon. The possible role of the resulting π-complexes in electrophilic substitution reactions has been exhaustively discussed in the literature (see, for example, Refs. 136 and 137). A great deal of work[138,139] has been done on the ArH–HX–MX system, where X = halogen.

Recent work[140-144] has led to the hypothesis that the π-complexes of aromatic hydrocarbons with metallic or oxidic catalysts can play the role of intermediates in catalytic reactions. Thus, Völter[143] suggests that the hydrogenation of alkylbenzenes on Ni–MgO catalysts involves the formation of π-complexes between the hydrocarbon and the catalyst, which are then hydrogenated by adsorbed hydrogen atoms.

Existing data are not sufficient to justify a definite conclusion on the role of CTI in determining the reactivity of aromatic hydrocarbons. We may assume that the effect does occur, and results in a slight decrease in reactivity towards electrophilic reagents. Data on the chemical reactivity of complexes of the ferrocene and dibenzene-chromium type are of little help, because we still lack general rules as to the behaviour of these compounds[145-147]. Thus, ferrocene is more reactive than benzene towards electrophilic substitution, a behaviour diametrically opposite to that of the dicyclopentadienyl complexes of other metals.

Jones and coworkers[148-153] studied the effect of coordination on the reactivity of aromatic ligands containing nitrogen or oxygen atoms. The reaction rate was significantly affected by complex formation in only a few cases. Thus, a study of the rate of nitrogen coupling of 8-quinolinol-5-sulphonic acid and of its Zn^{2+} complex showed[151] that the free phenate ion reacts 10^4 times faster that the same ion coordinated to the zinc ion, but the latter is significantly more reactive than the undissociated ligand. Inner complexes of 8-quinolinol with Fe^{3+}, Cr^{3+}, and Co^{3+} are brominated 35 times faster than the free ligand[153]. On the other hand, it is stated[148] that the activity of aniline and pyridine towards electrophilic reagents is the same whether the bases are free or coordinated to Cr^{3+}. Jones' general conclusion is that coordination of simple aromatic ligands has a relatively minor effect on their reactivity towards electrophilic agents. Two papers[154,155] are quoted in support of this conclusion. In the former, the $\pi-\pi^*$ transition in the electronic spectrum of pyridine is shown to be relatively insensitive to coordination. In the latter, the π-electron density on the atoms of the porphin ring was calculated and shown to be little influenced by complex formation with Fe(II)

Jones also concluded[152] that the direction of electrophilic substitution reactions of aromatic compounds is not affected, as a rule, by coordination. The present writers consider, however, that coordination can influence the isomeric composition of the products of electrophilic substitution when both species involved in the reaction can undergo CTI with the catalyst. The reaction between phenol and formaldehyde discussed above (p. 484 of Russian; p. 11 of translation) is an example of this type of behaviour.

Hydrogen halides. Coordination increases the polarity of the bond in the hydrogen halide (HX) molecule. The cations of many metals, and in particular those of the platinum group and of the copper and zinc subgroups, can coordinate to HX with formation of $H_n[MX_m]$ acido-complexes, in which the hydrogen is located in the outer sphere of the complex as a proton[15-17,19,156,157]. Complexes of this type are formed not only in solution, but also in molten salts[158,159], and on surfaces[12,46].

Ahrland[160] suggested the formation of a dative π-bond between M and X, by the interaction between the d-electrons of the metal and the free d-orbitals of the halogen, in order to explain many experimental observations on the stability of halogeno-complexes[16,18]. This hypothesis is consistent with the report[157] that the cations of certain metals (alkali, alkaline-earth, tervalent rare-earth, and some others) which have no mobile d-electrons cannot readily form negatively charged complexes with the chloride anion. On the other hand, cations prone to dative interaction (e.g. Pt, Pd, Hg, Ag) form complexes of this type over the whole of the HCl concentration range.

The polarising and weakening effect of CTI on HX molecules is relevant to the catalysis of many reactions involving hydrogen halides. We may mention, as an example, the hydrochlorination reactions of acetylene[47,49,51] and methanol[98], catalysed by Hg^{2+}, Cd, Zn, and Bi chlorides.

Carbon monoxide. The drastic change in reactivity resulting from the coordination of carbon monoxide was first observed by Hieber and coworkers[161,162] in the early 1930's. The ease of oxidation in particular, of CO is very much increased by coordination. The following are typical reactions:

$$PtCl_2CO + H_2O \rightarrow Pt + CO_2 + HCl$$
$$Fe(CO)_5 + 2NH_3 + H_2O \rightarrow H_2NCOONH_4 + H_2.$$

According to currently-held views, CO takes place in CTI not only as a donor but also as an acceptor of electrons[24,163,164]. Dative interaction, made possible by the free antibonding π-orbitals of the ligand, contributes very significantly to the stability of the resulting carbonyl complexes. This is confirmed by the fact that carbon monoxide forms complexes with many transition metals but not with the usual acceptors of unshared pairs such as BF_3.

Coordination of carbon monoxide decreases the stability of the C–O bond. Thus the C–O stretching vibration frequency is significantly lowered on going from free carbon monoxide to carbonyl complexes[75,164]. The dative component contributes significantly to the loosening effect of CTI on the C–O bond. Markov and Fasman[165] studied the mechanism of the catalytic activation of CO in solutions, and concluded that dative interaction between the metal and carbon monoxide is one of the necessary conditions for activation.

The influence of CTI on the reactivity of carbon monoxide is shown by the many catalytic reactions involving metal carbonyls (e.g., oxo-synthesis reactions).

Nitrogen. The activation of molecular nitrogen due to CTI is discussed at length in a recent review article by Vol'pin and Shur[166].

Oxygen. The possibility of CTI between metal ions or atoms and the O_2 molecule has been considered by many authors[9,11,68,163]. According to Jones[11], activation of molecular oxygen by coordination should be widespread in inorganic and in biological systems. He suggests that

the cations which are most active in this respect are characterised by a tendency to form π-bonds and to transfer an electron to the oxygen. These properties are found in Fe^{2+}, Mn^{2+}, Co^{2+}, and Cu^{+}.

A coordinate bond involving a dative component can be realised in the ions FeO_2^{2+} and CuO_2^{+}, which play an important role as oxygen carriers in the activity of some enzymes[168]. Orgel[24] mentions oxyhemoglobin, oxymyoglobin, and other biologically important compounds of iron, copper, and cobalt as examples of oxygen-containing complexes. Griffith[169] considers the bond between O_2 and iron in the hemoglobin complex to be similar to the Pt–ethylene bond in the Zeise salt (see Refs. 74 and 104).

It can be assumed that an oxygen molecule is held by a coordinate bond in the molecule $[IrCl(CO)O_2(PPh_3)_2]$, where $Ph = C_6H_5$. The structure of this product, prepared by Vaska[170] by treating the complex $[IrCl(CO)(PPh_3)_2]$ with molecular oxygen, has been investigated[171]. The oxygen atoms were found to lie at the same distance from the iridium atom, the length of the O–O bond (1.30 Å) being close to the distance between oxygen atoms in the O_2^- ion (1.28 Å).

Hydrogen. The activation of molecular hydrogen by metal ions has been discussed in a number of papers[172-176]. Interaction between an H_2 molecule and a metal ion or atom may involve attraction of the electrons from the hydrogen towards the free orbitals of the metal, and dative interaction between the d-electrons of the metal and the antibonding orbital of the hydrogen[163,177]. Strictly speaking, only the latter should be termed CTI, since the σ-electrons of the H_2 molecules are involved in the former.

Bykhovskii and Temkin[177] consider dative interaction to be an essential part of the mechanism of molecular hydrogen activation in homogeneous catalysis. Arguing against Halpern's suggestion[172] that the activation of H_2 is determined primarily by the electron-acceptor properties of the metal, these workers point out that the bond order in the H_2 molecule and the H_3^+ and H_3^- ions is consistent with a considerable loosening of the H–H bond, resulting from the transfer of an electron to the antibonding orbital of the hydrogen molecule. Gupta's[178] quantum-mechanical calculation for the H_2^- ion lends support to this view.

Hydrido-complexes, such as $[IrH_2Cl(CO)(Ph_3P)_2]$ [179] and $\{PtHCl[P(C_2H_5)_3]_2\}$,[180] have recently been prepared. The nature of the metal–hydrogen bond in these compounds is evidently the same as in covalent metal hydrides[179]. According to Halpern[174], the mechanism of the catalytic activation of hydrogen often involves the formation of intermediate hydride complexes in which the hydrogen can be treated as an anionic ligand.

III. INFLUENCE OF LIGANDS ON THE CATALYTIC ACTIVITY OF METAL IONS

The catalytic properties of a metal ion are often substantially influenced by the nature of the ligands. Halpern[173] has obtained data which characterise the relative influence of various complexing agents on the activity of the Cu^{2+} ion in homogeneous hydrogenation reactions (see Table).

It is reported[181] that the reactivity of platinum complexes towards the CO oxidation reaction decreases along the following series of ligands:

$$I > Br > CNS > Cl > NO_2 > OH > NH_3 > CN.$$

Replacement of the chloride by the citrate anion in the coordination sphere of the Ru^{3+} complex causes a significant increase in the catalytic activity of the complex towards the oxidation of ethylene and acetaldehyde[182].

Terent'ev and Mogilyanskii found[183-185] that aromatic amines in a pyridine solution in the presence of Cu_2Cl_2 are oxidised by atmospheric oxygen to diazo compounds. The catalyst in this case is a pyridine complex of the copper salt. On replacing the pyridine by 2-methylpyridine the reaction proceeds much more slowly, and if quinoline, dioxan, or alcohol are used as solvents no oxidation is observed.

Influence of complexing agents on the catalytic activity of the Cu^{2+} ion.

Agent	Relative catalytic activity	Agent	Relative catalytic activity
Perchlorate	1	Sulphate	6.5
Butyrate	150	Chloride	2.5
Propionate	150	Glycine	0.5
Acetate		Ethylenediamine	0.1

The nature of the ligands has a particularly strong influence in the case of enzymes and their models. The catalase activity of lead ions complexed with various Schiff's bases is almost 300 times higher than the activity of the simple lead ion[186]. The activity increases by several orders on going from the hydrated iron ion to an albumin–porphyrin complex of iron[187]. Many examples of this type are quoted by Langenbeck[188] and Nikolaev[189,190].

Often the nature of the ligand affects the direction of the reaction as well as the activity of the metal-containing catalyst. The emulsion polymerisation of butadiene in the presence of K_2PdCl_6 gives mainly a 1,2-polybutadiene structure, whereas the 1,4- polymer is the main yield when PdI_2 is used as catalyst[191]. Depending on the coordination sphere of the nickel complexes used as catalysts the polymerisation of acetylene can yield benzene or cyclooctatetrene[192].

To explain the influence of ligands on the catalytic properties of complexes, several factors must be considered. The tendency of catalysts to form complexes with ligands, and the influence of CTI on their reactivity, are determined first and foremost by the acceptor and donor properties of the metal ion. Hence, these properties must also to a large extent determine the catalytic activity of the complex. The nature of the metal–ligand bond has a profound effect on the donor–acceptor properties of the central atom. As the ionicity of this bond increases, the acceptor tendency of the metal ion increases and the donor tendency decreases. Formation of dative bonds increases the positive charge on the central atom and thus enhances its acceptor properties.

In mixed complexes, the ability of some of the ligands to undergo dative interaction results in a loosening of the dative bonds between the metal and the other ligands. In this case, the ligands are competing for the d-electrons of the metal. If dative interaction is needed to activate the reagents, a good catalyst will not include ligands capable of forming dative bonds.

These considerations can be used to analyse the effect of the carrier on the activity of the catalyst when CTI between the metal ion (or atom) and the carrier can be assumed. We have used this approach[12,49,51,52] in our work on vapour-phase addition reactions to acetylene to explain the fact that salts are more active when deposited on carbon than on other carriers. We were able to conclude that carbon, as a ligand, can enter into donor–acceptor interaction with a metal ion, playing the part of an electron donor. As a result, the donor properties of the cation and its tendency to undergo dative interaction are enhanced: this is a very significant factor in determining the activation of acetylene.

The crystal field theory can be used to discuss the role of the carrier. Erofeev and coworkers[193] have suggested an interaction between the atoms or ions of the deposited metal and the crystal lattice of the carrier, resulting in penetration of the metal ions into the surface layer of the carrier. On this assumption, they were able to explain why γ-Al_2O_3 is the best carrier for nickel hydrogenation and dehydrogenation catalysts and for chromium oxide dehydrocyclisation catalysts. The structure of γ-alumina is such that the Cr^{3+} and Ni^{2+} ions find themselves in an octahedral field, which offers a higher stabilisation energy than fields of different symmetry.

Unusual oxidation states for particular metals can often be stabilised by complex formation. Thus, complexes of Cu^{3+}, Ag^{2+} and Ag^{3+}, Ni^{+}, Cr^{5+}, Pt^{3+}, Pt^{5+}, Pt^{6+}, Pt^{8+}, have been shown[194-196] to exist with certain ligands. In these complexes, the donor–acceptor properties of the metal atom can differ very substantially from those of the same atom in its usual valency states. Several instances of catalytic activity have been reported for metals in unusual oxidation states. Rich and Taube[197] showed that a number of isotope exchange reactions are catalysed by Pt^{2+} and Au^{2+} compounds. It has been pointed out[198] that Cr^{5+} ions are the active centres of chromium oxide polymerisation catalysts.

Once it is established that a particular oxidation state of a metal shows maximum catalytic activity, the factors which contribute to the stabilisation of this state can be evaluated. Ligands tending to form dative π-bonds stabilise the lower oxidation states[24]. The effect of the nature of the ligands on the stability of the states of a metal ion with a different number of d-electrons can easily be evaluated in the crystal field theory approximation. For example, the Cr^{5+} state, in which the ion has one d-electron, is stabilised by the ligand field. Cr^{6+}, on the other hand, has no d-electrons, and the stabilisation energy for this state is zero. Hence, the stability of the Cr^{5+} state increases with the strength of the ligand field.

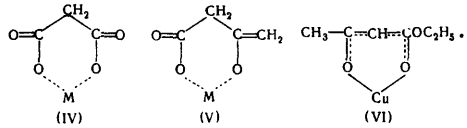
In all probability, the ligands themselves often participate directly in the catalytic process. Taube[199-201] believes electron transfer through a ligand bridge to be a possibility in oxidation–reduction reactions, and Stranks[195] considers this to be the most likely mechanism for the Cr^{2+}–Cr^{3+} system. Matveev and coworkers[133] believe that the oxidation of the Pd^0 complex by the Cu^{2+} ion during the catalytic oxidation of ethylene to acetaldehyde occurs through a bridging complex, and that electron transfer from ion to ion is accompanied by the transfer of a ligand. They point out that the oxidation is fastest when the ligand being transferred has an unshared electron pair.

Coordinated ligands can form hydrogen bonds with other molecules[74]. This effect can be important in controlling the orientation of reacting molecules, particularly in enzyme catalysis[32].

IV. COORDINATION INTERACTION AND CHARACTERISTICS OF THE TRANSITION STATE OF CATALYTIC REACTIONS

Several attempts have been made to use complexes as models of the transition state. Hammond[202] formulated the following postulate: if the transition state and the intermediate complex are formed consecutively during the reaction and have similar energies, their molecular structures can be expected to be similar. Since complex formation is an exothermic process, the postulate implies that the transition state and the intermediate complex can have similar structures only when the activation energy of the reaction is low.

The parallelism between the reaction rate and the stability of complexes is often interpreted as evidence for a similarity in structure between the complex and the transition state. Prue and Hoppe[95,203] suggested that the catalytic activity of metal cations towards the decarboxylation of acetonedicarboxylic acid and the hydrolysis of dicarboxylic acid and aminoacid esters depends on the mode of chelation of the activated complex in these reactions. They based this conclusion on the good correlation between the activity of various metal cations and the stability constant of the complexes of these metals with malonic acid. The structure of these complexes and the proposed configuration of the transition state for the decarboxylation of acetonedicarboxylic acid is shown by formulae (IV) and (V):



According to Bell[204], the transition state during the bromination of ethyl acetoacetate in the presence of copper ions is stabilised by a metal cation in a form similar to that of the chelate complex (VI).

The crystal field theory has made possible a new approach to the characterisation of the transition state. Several papers[7,18,23,24,205,206] have dealt with the activation energy of ligand replacement reactions in complexes. The transition state was treated as a complex in which the number of ligands per reacting unit is smaller (S_N1 mechanism) or greater (S_N2 mechanism) than in the starting complex. By assuming a specific steric configuration for the activated complex it is possible to estimate the change in the crystal field stabilisation energy attending the change from the starting complex to the activated complex. The result is one of the terms which make up the activation energy. tion energy.

The same approach can be applied to catalytic reactions. Dowden and Wells[207] applied the crystal field theory in their analysis of the catalytic activity of various metals, oxides, and sulphides. Unsaturated valencies on the surface of the catalyst were treated as empty sites in the coordination sphere of a complex having one of the surface cations as its central ion. A change in the coordination of the surface complex takes place during formation of the transition state of the limiting step, which includes adsorption. For example, a square pyramid changes to an octahedron, and a tetrahedron changes to a square pyramid. Under these conditions, the stabilisation energy due to the crystal field of the transition state will differ for the various catalysts according to the number of d-electrons in the metal. In this way, the authors were able to explain why the minimum activity in H_2–D_2 exchange reactions and in some

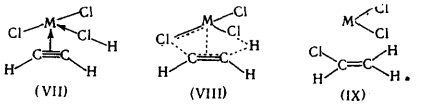
oxidation–reduction reactions is found with catalysts containing cations with d^0, d^5, and d^{10} electronic configurations, for which the stabilisation energy is zero. At the same time, the d^3 and d^7 systems (in which the stabilisation energy attending the formation of the activated complex is greatest) showed the maximum catalytic activity.

Krylov[208] points out that the opposite relationship should be observed when formation of the transition state involves a decrease rather than an increase in the coordination number. In this case the stabilisation energy due to the crystal field will decrease, as a rule, on formation of the transition state, and the highest catalytic activity will be found in d^0, d^5, and d^{10} systems. Catalysts of this type have been shown to be the most active in the polymerisation of ethylene oxide on metal oxides and hydroxides, in the dehydration of formic acid, etc.

Glasstone, Laidler, and Eyring[209] state that the transition state of many reactions can be expected to be similar to the final state. Hence, and in view of the important role of mixed complexes in catalysis discussed above, we may conclude that the transition state of many bimolecular reactions of the type

$$A + B \xrightarrow{K} \text{reaction products}$$

has a configuration intermediate between the final state and the mixed complex AKB. For example, the hydrochlorination of acetylene on MCl_2 salts[47] has been described by the following formulae for the mixed complex (VII), the proposed activated complex (VIII), and the final state (IX):



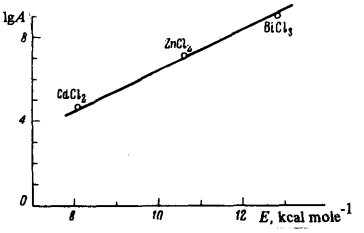


Figure 2. Compensation effect in the catalytic hydrochlorination of acetylene.

Structures (VII) and (VIII) can serve as an illustration of the present writers' suggestion[12,51] that the interaction between the catalyst and the reagent in the transition state can be similar to the interaction between the metal and the ligand in the corresponding complex. This hypothesis allows us to characterise the transition state in terms of data on the influence of CTI on the ligands, and to establish a relationship between the parameters of the metal ion which are important in coordination and the characteristics of the transition state of a reaction catalysed by the same ion. For the reaction

$$MCl_n \cdot C_2H_2 + HCl \rightarrow CH_2{=}CHCl + MCl_n \cdot$$

we had previously determined[47] the pre-exponential factor (A) and the activation energy (E). We found that both A and E increase along the series of catalytic salts $HgCl_2$–$CdCl_2$–$ZnCl_2$–$BiCl_3$, in which the acceptor properties of the cation increase and the donor properties decrease[12,49,51]. The relationship between lg A and E is accurately linear for the chlorides of Cd, Zn, and Bi (Fig. 2). Similar results were obtained for the catalytic synthesis of vinyl acetate from acetylene and acetic acid[48], and for the hydrochlorination of methanol[98]. Thus, at least some reactions show a definite relationship between the Arrhenius parameters and the donor–acceptor properties of the catalyst. This dependence may sometimes give rise to a compensation effect, since an increase in acceptor properties along a series of similar catalysts is usually accompanied by a decrease in donor properties. The decrease in activation energy accompanying an increase in the donor tendency of a catalyst can be explained by the drastic loosening effect of dative interaction on the reactant molecule[12,41–43,49,51,177,210].

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*This may well be a reference to "Die organischen Katalysatoren und ihre Beziehungen zu den Fermenten", Berlin, Springer Verlag, 1949.

**[The author probably has in mind p. 398 of this reference (Ed. of Translation)].