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Organic Reagents in Spectrophotometric Analysis

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The spectrophotometric analytical methods using organic reagents in modern chemistry are discussed. Certain new organic reagents, synthesised in recent years, are presented. New methodological procedures in spectrophotometric analysis and the possibilities of the available apparatus are examined. The advances achieved in the development of the theoretical principles of the action of organic reagents are described and a new approach to the explanation of the reactivity of organic compounds is put forward.
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I. INTRODUCTION

The spectrophotometric methods are virtually the commonest methods in chemical analysis. Colour reactions of practical value have now been found for almost all inorganic ions. An increasing number of organic analytical methods are based on the corresponding colour reactions. The principal advantages of spectrophotometric methods is high sensitivity, universality (i.e. the possibility of determining both small and large amounts of substances), simple apparatus, and the possibility of automating the analytical procedure.

Spectrophotometric analysis is based on organic reagents (OR), whose number has been continuously increasing. At the same time the efficiency of their analytical action has increased: OR forming complexes with unusually high extinction coefficients of the order of several hundreds of thousands have appeared, which makes it possible to determine reliably 0.01 mg ml^{-1} of an element or even smaller amounts. The wide-scale automation of the methods requires the development of direct and rapid analytical procedures. This depends mainly on two factors: the selectivity and reliability of the reactions. By reliability, one understands the independence of the results of slight changes in reaction conditions and also only a slight influence of other substances present in solution on the main reaction. The most reliable results may be expected when OR interacting with the elements in acid media and not requiring the application of buffer solutions are used. The procedure employed in preparing the solution for the photometric measurements then reduces to simple dilution of the analytical solution with an acid (which, for example, makes it possible to carry out the analysis in a stream of liquid); furthermore, the possible interference associated with the hydrolysis of the ions and the formation of polymeric structures is reduced, which is especially important in the determination of certain rare and other, mainly heavy, readily hydrolysable elements such as Ti, Zr, Hf, Nb, Ta, and Pa. A series of effective OR which can be used in highly acid media have been proposed in recent years: arsenazo III and its analogues; antipyrine and its numerous derivatives; reagents of the triphenylmethane series; fluorones; azo-compounds based on pyrogallol, pyridine, and heterocyclic reagents, as well as many other groups and classes of OR.

A series of monographs[1-30] have been devoted to the theory and practice of the application of OR in photometry. These studies dealt with questions of the synthesis of the OR, their purification, and analysis,[8,12,20,27,28] the classification of the OR and the creation of an assortment of the latter suitable for individual elements,[2,7,9,12,15,20,23-25,29,30] the use of OR in spectrophotometric and luminescence measurements,[3,5,6,9,10,15,16,20,22,25] their use for the determination of organic substances[1] and anions,[21] and their application in ultra-microanalysis[4] and in extraction,[14,18] and also questions concerning the theory of the action of the OR.[2,7,8,9,20,23,24,26]

In the present review we shall confine ourselves to the consideration of the OR employed only in spectrophotometric and luminescence measurements. Attention is concentrated on azo-derivatives of chromotropic acid, because results important for the development of the theory of the action of OR have in fact been obtained in recent years precisely for these practically important OR. These results can be in many cases extended to other classes of OR.

II. PRINCIPAL CHARACTERISTICS OF THE COLOUR REACTIONS

The OR are organic compounds (monomeric or polymeric) of different classes which are used for the qualitative or quantitative determination of chemical elements and compounds (inorganic and organic) and also for the separation, concentration, masking, and other auxiliary or preliminary operations preceding and accompanying the determination of substances by any methods.[31,32]

We shall consider several principal concepts characterising the properties of the OR and their metal complexes.

1. Contrast

Contrast is one of the important characteristics of a colour reaction, although this term has not been accurately defined in analytical chemistry and it is sometimes confused with reaction sensitivity. The reaction is said to exhibit contrast when two solutions, one of which contains the OR and the other the product of the analytical reaction, differ significantly in their colour under identical conditions.

A quantitative characteristic of the contrast of a colour reaction is the difference $\Delta\lambda$ (in nanometres) between the band maxima in the absorption spectra of the reaction product (MR) and the reagent (R): $\Delta\lambda = \lambda^{MR}_{max} - \lambda^{R}_{max}$. It is assumed that the reaction exhibits a low contrast if $\Delta\lambda < 40$ nm, a moderate contrast if $\Delta\lambda = 40-80$ nm, and a high contrast if

$\Delta\lambda > 80$ nm. It is also necessary to take into account the shape of the spectrum, in particular the half-widths of the absorption bands. If the absorption spectrum of the reaction product has two maxima, then $\Delta\lambda$ is usually calculated from the positions of the band maxima in the absorption spectra of the OR and the complex differing to the greatest extent. The presence of two maxima is characteristic, for example, of the OR of the arsenazo III group.

There are several possibilities for increasing the contrast of colour reactions. It is known that contrast for a reagent of the type of ROH can be enhanced by selecting a solvent promoting the elimination of a proton from the hydroxy-groups. Such solvents can be dimethylformamide (DMF) and dimethyl sulphoxide (DMSO), which are fairly strong proton-accepting solvents. This procedure is used, for example, to increase the contrast of the reactions of phenylfluorone and its analogues.[33]

A second way of increasing the contrast of colour reactions involves the change in the structure of the OR itself—in the simplest case the introduction of suitable substituents into the OR molecule. Usually these are electronegative groups: NO_2, Cl, Br. Alizarin S and many monoazo-compounds containing the *oo'*-dioxyazo-group, exhibit an increase in the contrast of their reactions with the elements after the introduction of the NO_2 group.

The problem of finding new OR giving rise to contrasting reactions with the elements is more difficult and has been less thoroughly investigated. In order to solve the problem of predicting the contrast of reactions, it is necessary to find the relation between the structural and analytical spectroscopic characteristics of the reagents and their complexes with the elements. The principal difficulty in the solution of this problem consists in the lack of a clear-cut mathematical definition of the characteristics of the contrast and also of the sensitivity, selectivity, and other analytical characteristics of colour reactions. The search for new or more promising OR is therefore at present prosecuted as a rule by comparing the properties of the OR of one or several chemical classes. An example is provided by the procedure whereby the contrast of the colour reactions of OR of the group of arsenazo III can be increased. By varying the substituents in the benzene rings, while retaining the main carbon skeleton of the OR molecule, it has been possible to synthesise more than 100 new OR; some of these are characterised by a very high contrast of their colour reactions.[20] For example, Dicarboxybenzene C, containing two carboxy-groups in the *ortho*-position relative to the azo-group, gives rise to colour reactions with copper ($\Delta\lambda$ = 106 nm) and manganese ($\Delta\lambda$ = 180 nm) in experiments in aqueous organic media (solutions in acetone and propanol). In order to achieve a high contrast, two factors are used in both cases: the choice of the optimum structure of the reagent and the application of non-aqueous solvents.[34]

In order to increase the contrast of colour reactions (and also in order to improve other analytical characteristics), one employs the procedure in which the elements are determined when they form part of the composition of heteroligand and heterometal complexes, which will be discussed in greater detail below.

2. Sensitivity

A series of procedures have been proposed for the quantitative expression of the sensitivity of colour reactions.[35,36] The most universal characteristic of the sensitivity is apparently the molar extinction coefficient ε† of the analytical reaction product. It is usually assumed that, when $\varepsilon < 2 \times 10^4$, the reaction is relatively insensitive, when ε reaches $(2-6) \times 10^4$ it exhibits a moderate sensitivity, and, when $\varepsilon > 6 \times 10^4$, the sensitivity is high. There exists a limiting value of ε ($\sim 2 \times 10^5$). Although reactions with $\varepsilon > 2 \times 10^5$ are known, these are as a rule cascade reactions.

The "apparent" (or average) molar extinction coefficient is a criterion of the sensitivity of the reaction. It is calculated from the familiar formula $\varepsilon = A/cl$, where A is the optical density of the solution to be analysed, c the concentration of the substance to be determined, and l the thickness of the solution for which photometric measurements are to be made. The conditions in the determination of the element are chosen empirically by selecting the pH or masking complex-forming substances which ensure the highest selectivity. One then considers the reaction mechanism, the yield of the coloured compound (which may be less than 100%), the possibility of the formation of ternary or other complexes, and the coexistence in solution of several coloured complexes. Consequently the apparent or average molar extinction coefficient characterises the sensitivity of the analytical method and its comparison with the true molar extinction coefficients provides an idea about the extent to which the sensitivity of the method of determination is reduced compared with the sensitivity of the reaction itself.

We shall consider the possible ways of increasing the sensitivity, drawing a distinction between the sensitivity of the analytical method and the sensitivity of the reaction itself. The sensitivity of the method can be increased by concentrating the element to be determined (for example, by extraction with organic solvents) or by increasing the thickness of the solution for which photometric measurements are to be made. In the method of spot tests there exist procedures whereby one can reduce by 1–2 orders of magnitude the limit of detection of absolute amounts of the test substances;[22] this also applies to the micromethods for the quantitative determination of substances.[4]

The sensitivity of the reaction depends in the first place on the properties of the OR and on the molar extinction coefficient of the reaction products. The reaction conditions (pH, the nature of the solvent, temperature, etc.) as a rule have an insignificant influence on the sensitivity of the reaction and determine only the yield of the reaction product, which is only rarely below 70–80% under the selected optimum conditions of the determination. Nevertheless it is well known that the character of the spectral curve (the position of the maximum and the intensity and half-width of the absorption band) can change following a change in the reaction conditions (pH and the solvent). This is due to the change in the character of the interaction of the OR with the metal: under new conditions, complexes having a different composition or structure are produced. For example, four different reaction mechanisms, which operate depending on the reaction conditions have been established for certain azo-dye reagents.[37] Application of the knowledge of these mechanisms combined with the appropriate alteration of the reaction conditions lead to one of the ways of increasing the sensitivity of the colour reaction.

3. Selectivity

The concepts of the specificity and selectivity of colour reactions have been examined in a number of studies.[38–41] By the term "selectivity of an organic reagent", we understand the range of the reactive components of the mixture to be analysed which can in principle interact with the given OR, giving rise to a colour reaction; by the term "reaction selectivity" we shall understand the range of the elements interacting with the given OR under certain conditions.

†Here and henceforth the coefficients ε are expressed in litre mol^{-1} cm^{-1}.

Methods for increasing the reaction selectivity are known. In the first place they involve the variation of the pH of the medium. In conformity with the theory of analogies,[42] colour reactions in acid media with oxygen-containing OR of the type of ROH are undergone only by elements whose cations exhibit an extremely high tendency towards hydrolysis: B, Pa, Nb, Zr, Hf, U(IV), Pu(IV), Th; apart from the elements already enumerated, colour reactions are undergone also by Al, Ga, UO_2^{2+}, PuO_2^{2+}, and Sc in moderately acid solutions, by the lanthanides, VO^{2+}, Mo, and Cu in weakly acid and neutral solutions, and by Zn, Ba, Sr, Ca, and Mg in alkaline solutions. The optimum (as regards selectivity) reaction conditions are determined by the nature of the OR and other factors, and in most cases the determination of readily hydrolysable elements in strongly acid media is more selective. Thus, allowance for the nature of the ions of the element constitutes an important factor in increasing the reaction selectivity.

Another universal method for increasing the selectivity of the determination involves the application of various masking substances, including complexones.[10,17] It is noteworthy that there is also a possibility of a scheme in which the element to be determined is masked. By measuring the optical densities of the solution before and after adding the masking substances, one can estimate the interference due to the presence of other elements (for example, UO_2^{2+} is masked by potassium hexametaphosphate in its determination with an OR of the arsenazo type).[20]

A promising method for increasing selectivity, which in due course may become universal, involves the determination of the element present as part of the composition of a mixed ligand complex. The number of publications concerning the development of this application has been increasing rapidly; we shall note only one of the latest monographs.[9]

The selectivity of the determination of an element can be increased by employing extraction-photometric schemes. Here one is not dealing with preliminary extraction and subsequent determination of the element but with the employment of the OR simultaneously for extraction and for photometric measurements. The method, which it has been possible to extend to virtually all OR of different classes, even those which are readily soluble in water, consists in extracting the diphenylguanidinium salt of the corresponding inner complex by butyl or pentyl alcohol with subsequent photometric measurements on the extract without any additional operations.[43,44]

The selectivity of the OR is determined by its structure and the nature of the functional-analytical group. Since the number of the possible functional groups is limited (approximately 100 groups have been described and investigated fairly adequately), much attention has been devoted to increasing the selectivity of OR with a specific group. Thus it has been observed[45,46] that the most general method of increasing the selectivity involves the introduction into the molecule of the reagent of substituents, generating steric hindrance to the formation of a complex, in the vicinity of the chelating centre. It has been noted[46] that the principal cause of the difficulty in achieving a high selectivity for the OR is the ability of metal ions to "become adapted" to the coordination requirements of the ligands. The Schwarzenbach principle (the maximum satisfaction of the coordination requirements of the given ion) is therefore inadequate and it is necessary to impose additional conditions for structural correspondence. As an alternative, the principle of at least the minimum satisfaction of the geometrical and donor–acceptor requirements of one ion combined with the maximum possible satisfaction of such requirements for all the other metal ions has been put forward.[47]

One of the most interesting and very promising procedures for achieving a high selectivity or even specificity of the reaction is the application of macrocyclic reagents in the cavities of which can accommodate only ions with specific coordination possibilities (see, for example, West[45]). An improvement of the selectivity of the OR can be achieved also by introducing into its molecule a second complex-forming group together with the main functional-analytical group.[48,49] An even more promising procedure for the creation of selective OR involves the synthesis of reagents with heterocyclic rings containing S, P, N, and other atoms.

For example, rhodanine was proposed at one time for the precipitation of Ag, Hg, Au, and other elements. However, the low solubility of rhodanine and of the products of its interaction with the elements and the low sensitivity of the reactions precluded its wide-scale employment in photometry. At the same time, by virtue of the enhanced reactivity of its methylene group, rhodanine reacts with compounds of different classes—aldehydes, ketones, and diazo-compounds, which has served as the basis for the synthesis of a series of new OR containing chromophoric groups. For example, 5-azo- and 5-condensed derivatives of rhodanine, its five-membered analogues (thiorhodanine, thiohydantoin, selenoisorhodanine, and 3-aminorhodanine), *N*-substituted 3-aminorhodanine derivatives, and the six-membered analogue thiopropiorhodanine, have been synthesised and investigated.[50–52] In terms of sensitivity and contrast, the azo-derivatives and condensed derivatives of rhodanine and its analogues are greatly superior to rhodanine itself. The most valuable analytical reagents proved to be azo-compounds containing aminosulphophenols as the diazo-components. In contrast to the condensed derivatives, the azo-compounds are more soluble and more stable in highly acid media. As a rule, these OR also give rise to more sensitive and contrasting colour reactions with the elements, in particular with the noble metals.

An appreciable excess of alkali, alkaline earth, and nonferrous metals does not interfere with the determination of the noble metals. It is possible to determine one element of the platinum group in the presence of others. This is achieved because of the difference between the optimum conditions for their determination (concentration, nature of the acid, and temperature) and especially by virtue of the different kinetic activities of different complexes of the noble metals, which depend on the nature of the ligands and on the oxidation state of the central atom in the initial complexes. Table 1 presents the conditions in the reactions and their sensitivities for two of the most interesting OR of this series.

Yet another way of increasing the selectivity of analytical reactions, unrelated to the change in the chemical structure of the OR molecule, is based on the use of its different tautomers.

Thus there exist fairly numerous ways of increasing the selectivity of colour reactions, some of which are fairly promising. At the same time there is as yet no universal criterion which would unambiguously indicate the procedure for the specific synthesis of OR specific for each element.

In conclusion of this section, we shall quote several examples of the spectrophotometric determination of anions using OR. Carminic acid ($\varepsilon = 5.7 \times 10^3$), dianthrimide ($\varepsilon = 1.8 \times 10^4$), and alizarin S (sensitivity 0.02 μg ml^{-1}) are most frequently used to determine boron.[53] The reagent dibromoarsenazo II makes it possible to determine boron in 85% sulphuric acid. The reaction exhibits an appreciable contrast ($\Delta\lambda = 110$ nm), sensitivity (0.01 μg ml^{-1}), and selectivity.[54]

OR belonging to the group of 2,7-bisazo-substituted chromotropic acid derivatives (indirect method) are most promising for the determination of sulphate ions.[21] The determination is carried out by a reaction involving the masking by sulphates of highly sensitive colour reactions between barium and the above OR. Among the numerous OR investigated, Orthanilic K has been recommended for the photometric and titrimetric determination of sulphates. In the photometric version it makes it possible to determine sulphate ions in the concentration range 0.03–1.5 μg ml^{-1}. The determination is carried out at pH 4 in 60% acetone or alcohol.[55] Analytical methods for a wide variety of materials have been developed and successfully employed: natural and industrial waters, air and gases, electrolytes, soils, mineral rocks, etc. The reaction is highly sensitive in relation to phosphate, arsenate, thiosulphate, and fluoride ions.

Table 1. The colour reactions of some platinum elements.[50–52]

Element	Reaction conditions	$10^{-4}\varepsilon$
Reactions of sulphochlorophenolazorhodanine		
Pt	3 *M* HCl	3.2
Pt	2 *M* H_3PO_4 + 2 *M* H_2SO_4	10
Rh	14 *M* H_2SO_4 + 6 *M* CH_3COOH	3.5
Ir	10 *M* H_2SO_4 + 6 *M* CH_3COOH	4
Pd	5 *M* H_2SO_4 + 8 *M* H_3PO_4	12
Au	1 *M* HCl	5.2
Ag	pH 8–10	2
Reactions of sulphochlorophenolazothiopropiorhodanine (thiorhodanine)		
Pt	5 *M* H_3PO_4 + 2 *M* CH_3COOH	6.5
Au	3 *M* H_2SO_4 + 3.5 *M* CH_3COOH	2.5
Ag	10 *M* CH_3COOH + 1 *M* H_3PO_4	5.3

Potentiometric methods with ion-selective electrodes and photometric determinations with OR are used nowadays to determine fluorides. In photometry the indirect methods for the determination of fluorides have been almost completely displaced by the direct determination of fluorides in the form of a three-component compound. It has been found that fluorides can be determined by reactions with zirconium and one of the reagents: arsenazo III, Sulphochlorophenol S,[56,57] Xylenol Orange, or Methylthymol Blue.[58] The difference between the rates of the reactions with the reagent of different forms of zirconium (complex fluoride and hydroxide) is used to determine fluoride ions. A direct linear dependence of the optical density of the solution on the fluorine concentration has been observed in the range 0.01–0.32 μg ml^{-1} for Xylenol Orange, 0.01–0.1 μg ml^{-1} for Chlorosulphophenol C, and 0.02–1.4 μg ml^{-1} for arsenazo III.[57,58]

Phosphates are in most cases determined by means of the formation reactions of reduced heteropolyacids. However, the possibility of the formation of different forms of heteropolyacids can lead to non-reproducible results; the selectivity of the reaction is low and so is its sensitivity: $\varepsilon = (2.1–2.7) \times 10^4$. The reaction with iron(III) ions in the presence of dithizon has been suggested for the determination of phosphorus (in the form of PO_4^{3-}).[59]

III. NEW METHODS FOR INCREASING THE EFFICIENCY OF SPECTROPHOTOMETRIC ANALYSIS

It is possible to differentiate at least three procedures for increasing the efficiency of the known analytical reactions: (1) the use of reactions involving the formation of multicomponent complexes; (2) the application of non-aqueous and mixed solvents as the reaction medium; (3) the use of surfactants in different versions of the reactions. These procedures refer to both colour and luminescence reactions and sometimes make it possible to increase the sensitivity by an order of magnitude and above, to shift the selectivity in the required direction, to improve the reliability of the analysis, etc.

1. Mixed-Ligand Complex Formation

Mixed-ligand complex formation, i.e. the transition from binary to more complex complexes containing three and more components, makes it possible to improve almost all the analytical characteristics of colour reactions. This method has been widely incorporated in practical chemical analysis from the 1950's onwards and has continued to develop.[9,60]

The importance of heteroligand complexes for analytical chemistry is due to their great variety, since mixed-ligand complexes constitute the most probable form in which ions exist in solution. All these equations have been discussed in detail in a monograph.[9] Heteroligand complexes are widely used in extraction–photometric analytical methods. Compounds of organic cations with metallochromic chelates constitute the most common group of compounds in the acid dye–metal ion–organic base systems. The role of the cations in such compounds reduces to neutralising the excess negative charges on the OR due to the presence of sulphogroups[45,61] or dissociated hydroxy-groups, which are not involved in chelate formation.[62,63] Analysis of the literature data has shown that more than 40 dyes are employed as metallochromic indicators, approximately 20 organic cations are used to neutralise the excess charges, and methods are available for the determination of more than 30 metal ions.[15,18,24,64,65]

Methods have been developed for the photometric determination of metals in the form of complexes with metallochromic reagents involving the introduction of quaternary ammonium salts into such systems.[9] The contrast of the reactions increases significantly in this instance. The use of four-component and more complex mixtures leads to new possibilities for the development of photometric and extraction-photometric analytical methods.

2. Organic Solvents in Photometry

One of the new methodological procedures in photometry, which makes it possible to improve the analytical characteristics of the known reactions and also to discover new reactions, involves the employment of organic solvents which not only constitute the medium for the photometric reactions but also influence significantly the reaction mechanism. The effects observed in photometry on passing from aqueous to aqueous organic or organic media are extremely varied. The sensitivity and contrast of the colour reactions and the rate of development of the colour increase, the composition of the complexes changes, and the complexes of elements in a particular oxidation state are stabilised. The observed wide variety of effects is due to the complexity of the processes

influencing the complex formation. Solvents displace tautomeric and acid–base equilibria involving OR, solvate in different ways both the reactants and the reaction products, alter the dielectric constant of the medium and the structure of the solutions, and influence the steric configuration of the complexes.

The application of organic solvents in photometry makes it possible to extend greatly the range of OR and masking complex-forming compounds. Solvents which are most readily available and are most miscible with water are usually employed in spectrophotometry: alcohols, acetone, dioxan, carboxylic acids, DMSO, and DMF. Studies have been made of the influence of solvents on the colour reactions of the elements with OR of different classes: with azo-compounds based on heterocyclic amines,[66,67] formazans,[68,69] and compounds of the triphenylmethane series.[70]

The influence of solvents on the reactions of the elements with 2,7-bisazo-substituted chromotropic acids and also with reagents of the triphenylmethane series has been investigated in detail.[71] A sharp increase of the sensitivity of the colour reactions of Ca, Sr, and Ba with OR belonging to the class of 2,7-bisazo-substituted chromotropic acids has been observed in aqueous acetone and aqueous propanol media.[71] Thus highly sensitive colour reactions of Sr and Ba with carboxynitrazo have been observed in water–acetone mixtures containing 40 and 80 vol.% of acetone respectively ($\varepsilon \cong 1.4 \times 10^5$, $\Delta\lambda > 180$ nm for both reactions),[72] while in a mixture containing 75 vol.% of acetone the reaction of Ca with Methanilic C takes place ($\varepsilon = 0.9 \times 10^5$, $\Delta\lambda \cong 110$ nm).[73] In acetone (containing less than 5 vol.% of water) and in propanol (<0.5 vol.% of water) there is a possibility of sensitive colour reactions for Ni, Co, Mn(II), and Cu.[74] Some of them, for example the reactions with carboxybenzene [Carboxybenzene S?] are characterised by a high sensitivity and contrast ($\varepsilon \cong 1.6 \times 10^5$, $\Delta\lambda > 180$ nm).

In aqueous organic media containing acetic acid, a sharp increase of the sensitivity and contrast of the colour reactions of Al, Be, Ga, and Ti with OR based on *c*-aminohydroxyphenols has been observed.[75] In the presence of H_3PO_4 and H_2O_2, aluminium and titanium form respectively ternary complexes which are not characteristic of other elements; there is a sharp increase of the rate of development of colour. The increase of the sensitivity and contrast of the colour reactions of Be with Chrome Azurol S has been observed in water–propanol mixtures.[76]

The increase of selectivity is determined both by the properties of the solvents (mainly their solvating capacity) and by the new possibilities for masking. For example, in acetic acid media the range of elements capable of giving rise to colour reactions is much more limited than in other solvents, which itself increases the selectivity. This may be associated with the fact that many elements form stable acetates, which entails the loss of the possibility of their interaction with the OR. For example, the selectivity of the colour reactions used to determine Be, Al, and Ti can be sharply increased by employing hydrogen halides (HF, HBr, HCl) as masking-complex-forming agents, which bind many interfering elements (In, Hg, and others) in anionic halide complexes and at the same time do not interfere with the reactions of Be, Al, and Ti. As a result, it is possible to determine Al, Be, and Ti in the presence of a more than 2000-fold excess of Ga, In, Zn, Bi, and other elements.[77,78]

The colour reactions of alkaline earth metals with OR belonging to the Orthanilic, Anthranilic and Benzene group in aqueous organic media are selectively masked by certain anions. Thus in aqueous organic media the sulphates selectively mask the colour reactions of Ba and Sr with Methanilic S, while oxalates mask the reactions of Sr with carboxynitrazo, which makes it possible to determine Ca in the presence of Ba and also Sr in the presence of Ca.[72] A difference in the masking of the colour reactions of Be and Al with Chrome Azurol S is observed in aqueous propanol media, which makes it possible to determine Be in the presence of Al.[76]

Highly sensitive reactions of Ni and Mn(II) with Carboxybenzene C or of Ti with nitrobenzene have been used to determine these elements in chloroform extract after the extraction of nickel by dimethylglyoxime,[79] of manganese by diethyldithiocarbamate,[80] and of titanium by cupferron.[81] The examples quoted by no means exhaust all the possibilities for the improvement of the analytical characteristics of the colour reactions using organic and aqueous organic media.

3. Application of Surfactants

The use of surfactants in photometric analysis is not a new application, but the most interesting results, both practical and theoretical, have been obtained only in recent years. The use of long-chain ammonium and pyridinium bases, namely cetyltrimethylammonium,[82] cetylpyridinium,[83] Zephiramine,[84] and poly-hydroxyethylated ethers of alkylphenols[85] had been described earlier. Water-soluble ionogenic and non-ionogenic surfactants are most suitable for analysis.

The salts of aliphatic primary, secondary, and tertiary amines, quaternary ammonium bases, alkylpyridinium, and a number of other nitrogen-containing bases such as imidazoline, imidazole, pyrimidine, oxazoline, and others behave as cationic surfactants. Cationic surfactants such as sulphonium, phosphonium, and thiuronium compounds are known. Alkanesulphonates, alkylarenesulphonates, alkyl sulphates, and related compounds containing additional polar groups (carbamide, ester, etc.) in the chain behaves as anionic surfactants.

Hydroxyethylated aliphatic acids, glycerol esters of stearic acid, esters of triethanolamine with organic acids and alkylphenols, hydroxyethylated high-molecular-weight alcohols, block-copolymers of epoxypropane and ethylene, polyethylene derivatives of alcohols, poly(ethylene glycol) derivatives of acid amides, amines, epoxypropane, etc. belong to the group of non-ionogenic surfactants.

The introduction of cationic surfactants, particularly those containing a quaternary nitrogen atom and the cetyl group, into a metal ion–OR system (at the appropriate pH) leads to a sharp increase of the contrast and sensitivity of the reactions. Highly effective methods have been developed for the determination of Be, Sc, Y, the lanthanides, Al, Ga, In, Ti, Zr, V, Nb, Ta, Mo, W, Mn, Fe, Co, Ni, Cu, Zn, Ge, Sn, Bi, Th, U, and other elements.[86–91]

Another analytical application of surfactants involves the determination of the percentage content of the OR in their preparations. The method is based on the formation of blue ionic associated species, basic triarylmethane dyes, and anionic surfactants.

Questions concerning the theory of these reactions, which are of interest for analytical purposes, have been discussed in the literature.[88–93] The mechanisms of the interaction of different types of surfactants are different. For example, it has been established that cationic surfactants and OR of the type of Catechol Violet react at a surfactant concentration below the critical concentration for micelle formation.[89–91] It has been suggested that compounds of the type of ionic associated species are produced. However, a sharp change in the colour of the solution indicates the interaction of the cationic surfactant via the hydroxy- and carboxy-groups and not via the sulpho-groups of the OR molecule. Thus the role of the surfactants reduces to exerting an additional influence on the π-electron system of the OR by forming an associated species via the oxygen of the free hydroxy-group, which entails a bathochromic shift of the long-wavelength absorption band.

A somewhat different picture is observed on formation of chelates of phenol-carboxylic acids of the triphenylmethane series. In the absence of surfactants, the formation of metal complexes via the carboxy-groups is characteristic of these OR.[94] The addition of cationic surfactants leads to the blocking of the carboxy-groups owing to the formation of associated species and to the transformation of phenolcarboxylic acids from polyfunctional OR to monofunctional OR, because only one complex-forming group, containing the phenolic hydroxyl and the carbonyl oxygen atom of the COOH group in the o-position relative to the hydroxyl remains available. Consequently the role of surfactants in relation to phenolcarboxylic acids of the triphenylmethane series presumably does not reduce solely to influencing the π-electron system of the OR; the character of the coordination of the metal atom also changes in the presence of the surfactant. The appearance of a narrow well resolved absorption band and the high extinction coefficient of the complex are determined by the characteristics of the structure of the first coordination sphere of the metal. The strong polarising action of the metal, the asymmetry of the OR molecule, and other features of the electronic structure of the complex are apparently of decisive importance.

When non-ionogenic surfactants are used, the mechanisms of their reactions with OR as well as with the complexes produced are somewhat different. The corresponding colour reactions are observed only after the attainment of the critical concentration for micelle formation with the surfactant, i.e. the corresponding processes probably take place in the micellar phase.[92-99] Such processes, involving the displacement of the equilibrium as a result of the local concentration of substances on the surface of the micelles, are known and have been combined under the term "micellar catalysis".

The use of surfactants in combination with OR is an example of the fact that the analytical possibilities are far from being exhausted even as regards well known reagents and the application of new ideas from related branches of science can significantly improve the principal analytical characteristics of large classes of OR.

We may note that significant advances in the development of the theory of all three principal methodological procedures (the use of heteroligand and heterometal complexes, non-aqueous solvents, and surfactants in spectrophotometry) already make it possible to carry out experiments designed to improve these methods in a purposeful manner and not at random and unsystematically. This is also promoted by the fact that the principal elements of the theories of all three methodological procedures have a single physicochemical basis—comprising vigorously developing ideas concerning surface and solvation effects, phenomena associated with hydrophobic hydration, structure formation in the solvents, and the influence of these phenomena on the tautomeric and acid–base equilibria involving the OR and ultimately on the mechanisms of the complex-formation reactions.[90,91,94,100]

IV. THE CHOICE OF ORGANIC REAGENTS FOR THE DETERMINATION OF INDIVIDUAL ELEMENTS

By virtue of the advances in their synthesis, the number of OR proposed for the determination of individual elements has continuously increased and has already reached several thousands. The principal difficulty facing the analytical chemist is not the search for OR for the determination of a particular element but the selection of the best OR among many others. It is not always clear from the literature whether a newly described compound is the most effective OR for the given ion or whether the author investigated the given compound together with others, which are frequently analogues of a known OR, in order to obtain a more complete picture of the interaction of OR having similar structures with metal ions. Much attention has therefore been devoted in recent years to studies designed to obtain comparative analytical data characterising the efficacy of various OR in the determination of individual elements.

The principal characteristics which must constitute the basis of the selection of the reagents are (1) sensitivity, which can be expressed in terms of the molar extinction coefficient or with the aid of other parameters, (2) stability of the reaction product expressed in terms of the stability constant, (3) the limiting dilution or the observation limit, which are associated with the above two quantities, (4) selectivity with respect to anions, and (5) the pH necessary for the maximum yield of the complex (as a rule the more valuable OR make it possible to determine the elements in a more acid medium). The contrast of the colour reactions $\Delta\lambda$, the influence of the reagent (as the background substance) at the optimum (working) wavelength ($\varepsilon_{MR} - \varepsilon_R$ or $\varepsilon_{MR}/\varepsilon_R$ at λ_{opt}), the selectivity in relation to cations, and also the rate of equilibration, the stability of the OR and the reaction product with respect to the action of oxidants, reductants, and other external influences, the extractability of the complex, etc. are no less important characteristics.

Table 2. Examples of group reagents for the photometric and extraction-photometric determination of the elements.

Reagent	Elements
Chrome Azurol S	Be, Al, Ga, Zr, Th, Fe, V, Cu, Mn, Sn, Ti
Antipyrine C	Be, Ca, Cu, Ni, Zn, La, Ge, U(VI), Th, Al, Ga, In, Zr, Sc
Arsenazo I	U, Th, Zr, Sc, Ln, Al, Be, Ti, Nb, V, In
Arsenazo III	Th, Zr, Hf, Np, Pu, Pa, U, Sc, Ln, Pd, Ca, Pb
Arsenazo M	Ln, Cu, Pb, Ca, Sr, Th, Ba, Bi, Zr, Hf, Mg, Al, Zn, Cd, Ga, In, Mn, Ni, Ru, V
Dithizone	Pb, Zr, Cd, Hg, Ag, Cu, Bi, Pd, Mn, Fe, Co, Ni
Sodium diethyldithiocarbamate	Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ru, Pd, Ag, Os, Ir, Pt, Au, Tl, Bi
Xylenol Orange	Al, Be, V, Ga, Zr, Fe, Cd, In, Cu, Mo, Nb, Sn, Pd, Pb, Tl, Ti, Th, Bi, U
Methylthymol Blue	Al, V, Ga, Fe, In, Ln, Ca, Mg, Mn, Cu, Ni, Pb, Ti, Th, Zr, Zn
Pyridylazoresorcinol	Nb, Ta, Co, Pd, In, Ga, Ln, Cu, Zn, Cd, Tl, Sc, Th, Pb, Bi, U
Sulphochlorophenol S	Nb, Zr, Sc, Mo, Al, Ga, In, Cu, V
Thoron I	Th, U(IV), Zr, Be, Se, Pu, Np

The selectivity of the OR is one of the most important criteria of its analytical value. However, the number of specific or highly selective OR is extremely limited. The creation for each element of an assortment of OR which mutually supplement one another as regards selectivity has been increasingly considered in studies of recent years. Depending on the assumed content of other interfering elements in the object to be analysed, a specific OR is employed or, if possible, one OR is used for the separation of the element and another for its determination. For example, arsenazo III and Sulphochlorophenol S are mutually complementary OR for the determination of zirconium. Arsenazo III makes it possible to determine zirconium in the presence of niobium, molybdenum, and copper, but thorium, uranium, and the lanthanides greatly interfere with the successful outcome of the analysis. On the other hand, Sulphochlorophenol S makes it possible to determine zirconium in the presence of thorium, uranium, and the lanthanides, whereas the presence of niobium, molybdenum, and copper interferes with the analysis. Such pairs of OR can be selected

from many elements. If the solution to be analysed is complex and contains a wide range of elements or if its composition is not known beforehand, then one of the complementary OR can be employed to isolate the element to be determined (for example, by extracting zirconium together with niobium, molybdenum, and copper) and then zirconium is determined in the extract with arsenazo III; the elements isolated together with zirconium do not then interfere with the analysis.

The creation of an assortment of OR for the determination of each element makes it possible to confine oneself in analytical practice to the wide-scale employment of only some of the OR synthesised–group reagents, each of which is in principle suitable for the determination of several elements. The advantage of using a limited number of group OR in analytical practice is that they can be investigated comprehensively and a rational scheme can be selected for the determination of each element. Table 2 presents some of the most important group OR used for the spectrophotometric determination of the elements as well as the elements with which they can give the most characteristic colour reactions. The creation of a rational assortment of OR for the determination of individual elements constitutes a complex and fairly laborious task, because it is then necessary to take into account numerous factors both scientific and industrial. In the USSR such investigations are being prosecuted by several groups of investigators.[6,7,15,18–21,23–27,29,101–117]

V. DEVELOPMENT OF THE THEORETICAL PRINCIPLES OF THE ACTION OF ORGANIC REAGENTS

The studies which are being carried out on the theory of the action of OR can be as a rule assigned to three classes: (1) the determination of reliable thermodynamic and kinetic characteristics of the processes leading to a specific analytical effect; (2) the study of the mechanism of complex formation, i.e. the determination of the consecutive steps in the formation of the reaction products, and the elucidation of the structures of the OR and the final reaction products under different conditions; (3) direct study of the effect which determines the analytical value of the OR, i.e. the nature of the colour reactions in the case of OR for photometry, luminescence, etc.

The question of the structure of the OR and their complexes with the elements is the basis of all subsequent theoretical constructions associated both with the explanation of the analytical effects of the given OR and with the possibility of predicting to some extent the properties of new OR. Babko noted[16] that the structural formulae of the complexes of the elements, even those with known OR, frequently exist as a "matter of tradition" and have been copied from one communication to another without due justification. This suggests a definite lag in the development of a general theory of the action of OR compared with the advances achieved in the field of their practical application. Indeed, even the determination of the classical structural formula constitutes a non-trivial task for many OR and their metal complexes.

The first investigations of Chugaev, Feigl, Belcher, and Kulberg, some of which have been mentioned in reviews,[32,118] are well known. Alimarin's studies have made a great contribution to the development of ideas about the functional groups in OR and about the relation between the structure and properties of the latter.[119,120] Later Kuznetsov developed a series of theoretical ideas, which explain the analytical action of OR: the range of elements forming complexes with reagents having a given structure (theory of analogies),[42,121] the mechanism of solid-phase colour reactions,[122] and intramolecular dissociation (ionisation).[123,124] The theoretical principles of the extraction-photometric method for the determination of the elements in relation to water-soluble complexes have been developed.[44,125,126]

Subsequent research concerned the investigation and explanation of the mechanism of the analytical action of arsenazo III and its analogues,[127] the theory of colour reactions of hydroxylated azo-compounds,[128,129] the study of acid dissociation[130] and protonation[131] of organic reagents, the determination of the relation between the reaction conditions and the properties of both the OR and the metal cation (the protonation constant of the reagent, the solubility product of the metal hydroxide, and the pH corresponding to 50% reaction),[132] and the determination of four types of colour reactions of organic reagents with elements differing in the structure of the complexes and their spectrochemical properties.[37,132–135] The theory of the action of azo-compounds as indicators has been investigated;[136] the theoretical principles of the employment of aqueous organic solutions as media for colour reactions have been developed;[74,100,137–139] the structure and properties of mixed-ligand complexes have been investigated;[140] atomic models have been used to establish the structure of OR and their complexes;[141] the structures of several complexes have been determined by EPR;[142] a new interpretation of the concept of the functional–analytical group of the OR has been proposed;[143] the kinetics of rapid colour reactions have been studied;[144,145] a theory of the application of surfactants in spectrophotometry has been devised.[86–96]

1. Chemical and Physicochemical Methods for the Determination of the Structures of Reagents and Complexes

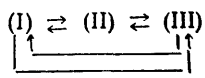
The physicochemical methods for the study of the structure of reagents and inner complexes of the elements with OR (spectrophotometry, EPR, potentiometry, and infrared spectroscopy) make it possible to obtain only indirect information about the structure of the given substance. Direct physical methods (X-ray diffraction analysis) are not applicable in all cases. Perhaps only the NMR method in its various versions, with its ever increasing instrumental capacity, may become in the immediate future a reliable and universal procedure for organic structural analysis.

The structure of the OR and its tautomeric and ionic states in the main determine the complex-formation processes and ultimately the analytical effect of the reaction. The difficulty of establishing the state of the OR and the structure of its separate forms is due to the fact that all the chemical and physical properties of OR are manifested integrally, i.e. can be caused by the simultaneous presence of a series of equilibrium forms.[146] The traditional physicochemical methods, including spectrophotometric methods, cannot always yield the required information. For example, the simplest aromatic azo-compound (azobenzene) has two stereo-forms: *cis*- and *trans*-azobenzenes.[147] These forms differ in their dipole moments and melting points; the steric differences between them have been established by crystallographic investigations. Analogous stereoisomers have been found for a series of substituted azobenzenes and azonaphthalenes.[148] Under specific conditions, one of the ionic and tautomeric forms of the reagent usually predominates. In this case the simultaneous application of spectrophotometric and potentiometric research techniques yields satisfactory results when an attempt is made to establish the sequence of stages in acid ionisation.[149] However, the data obtained must be treated as preliminary.

In general, allowance for tautomers, particularly for azo-compounds as OR, constitutes the most complex problem, which cannot always be solved by classical spectrophotometric

methods for the study of reactions. As an example, we shall consider the OR with the simplest structure—Acid Chrome Dark-Blue.[141,150] It is possible to imagine four equilibrium forms of only one ionic state of this reagent in 0.1 M H_2SO_4: (I), (II), (III), and (IV) (see below).

The existence of the reagent in the sole form (II) has been postulated[150] and the dissociation constant of this particular form has been calculated. The existence of the equilibrium (II) $\rightleftarrows$ (IV) has been postulated in another study[151] under the same conditions. Later quantum-chemical calculations demonstrated[152] that the state of the reagent in 0.1 M H_2SO_4 is described satisfactorily by the following scheme:

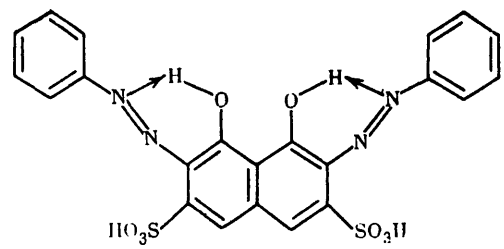


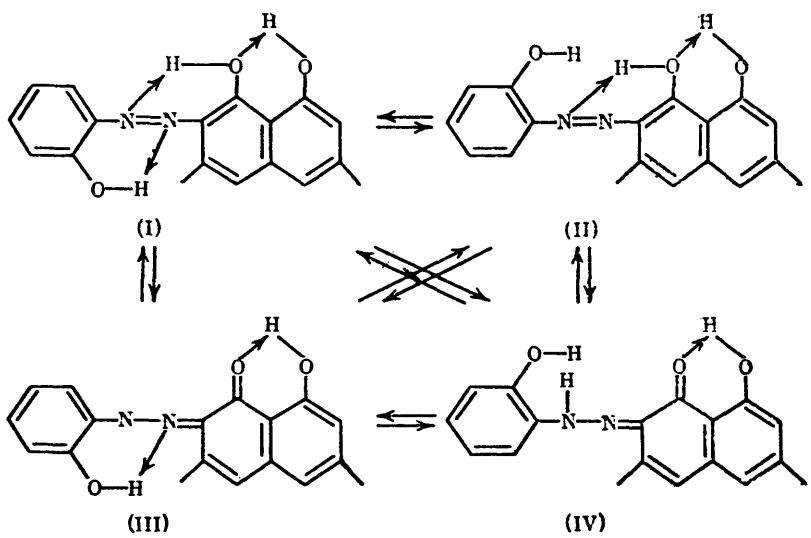
The phenomenon of tautomerism is well known but until recently such processes were considered only in isolated studies.[153,154] It was then usually assumed that the tautomeric equilibrium is almost wholly displaced towards one of the forms. Nevertheless, in determining the state and the characteristics of the reactivity of the OR, it is necessary to demonstrate in the first place the existence of one form or to estimate the concentrations of other forms, which, if they do exist, can interact with metal ions. It is known that the metal does not necessarily interact with the dominant form of the OR present in solution. The presence of metal ions can shift the equilibrium towards the formation of the complex with the form of the OR which would be less stable in the absence of the metal and would be present in solution at a low concentration. All these factors must be borne in mind in interpreting the mechanism of the complex formation reaction.

It is possible to quote a multiplicity of examples of the situation where different investigators have proposed several different structures for the same complex on the basis of the study of the latter by physicochemical methods. Other procedures, developed in recent years, which make it possible to obtain new information about the structure of the complexes and the reaction mechanisms and which have been developed in recent years, are considered below.

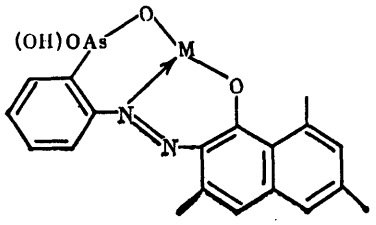
2. The Atomic Model Method

The method of atomic three-dimensional scale models, which has been used for a long time and extensively in theoretical organic chemistry, is in many instances very useful in determining the structure of OR and their complexes. For example, atomic models clearly show that, for OR which are azo-substituted derivatives of chromotropic acid, the only possible planar configuration is the *trans*-configuration of the molecule owing to the steric hindrance by the sulphogroups in the naphthalene nucleus. Thus, for example, the azo-form of the reagent, which is referred to as Benzene S, can be represented only by the following structure:



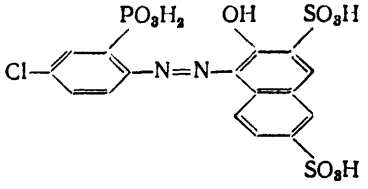


The method of atomic models made it possible to establish that the presence of bulky groups (AsO_3H_2, PO_3H_2, SO_3H, and even COOH) in the organic reagent in the o-position relative to the azo-group precludes the approach of the metal cation to the azo-group in the plane of the OR molecule and the metal ion must therefore be located somewhat above or below the plane of the molecule of the reagent.[141] For example, the structures of complexes of the type



which are usually put forward, are feasible in principle but only under conditions where the planes of the benzene and naphthalene rings have been rotated by ~25–30° and the metal atom is located above the plane of each ring. Only then is the closest contact achieved, within the limits of the sum of the average ionic radii, between the metal atom, on the one hand, and the atoms of the salt-forming groups and the nitrogen atom of the azo-group, on the other.

Three-dimensional atomic models make it possible to establish also other characteristic features of the structure of OR and their complexes. For example, it has been found[141] that, on interaction of a metal ion with chloro-phosphonazo P



the true structure of the complex having the composition MR_2 is one where the two molecules of the above OR are disposed around the metal ion with a coordination number of 6. In this case the molecule has a propeller structure; the planes of the benzene and naphthalene rings are parallel in pairs. In the molecule of the OR the angle between the planes of the two rings is 25–30°; the phosphono-groups are located on top, outside the plane of the benzene and naphthalene rings, while the metal atom is also outside these planes. Analysis of the model showed that another configuration, in which both azo-groups are in the same plane as the metal atom, can also be achieved. The above examples demonstrate the usefulness of the method of atomic models for the preliminary analysis of the possible structures and for deciding whether their existence is in principle possible or impossible.

3. Quantum–Chemical Methods for the Investigation of Colour Reactions

Quantum–chemical methods have been used for approximately 20 years in the study of complex organic reagents with specific features. They led to a way of solving certain important problems in the theory of the action of organic reagents which could not be achieved by the traditional methods available up to that time.[155–159] Thus Hückel's simple version of the quantum–chemical LCAO–MO method makes it possible to calculate the positions of the bands in the absorption spectrum of the OR and to estimate the total π-electronic energy of the system and the relative band intensities. The calculated characteristics of several structures obtained (the positions of the absorption band maxima and their intensities) have been compared with the corresponding experimental data and the structure is selected on this basis.

The LCAO method can also yield additional information about the electronic structure of the molecule of the OR and the complex: about the bond order (the amount of double bond character), about the π-electronic charges on the atoms, and about the free valence indices for individual atoms, i.e. it is possible to formulate the molecular diagram for the OR.

During recent years, extensive data have accumulated as a result of quantum–chemical studies of OR of different classes and their complexes with the elements. Apart from those already mentioned, we may also indicate several novel communications,[160–164] reviews, and monographs.[20,26,165] In the present review we would like to mention only certain features of the application of quantum–chemical methods, their scope, and the prospects for their further applications.

The structural complexity of many OR, the presence of several functional–analytical groups, and the possibility of tautomeric transformations and geometrical isomerism make the task of investigating the mechanism of the complex formation reaction and of the nature of the colour reactions extremely difficult. In calculations of the electronic and energetic characteristics of both the OR and the complexes, one therefore begins with a simplified model of these compounds. Since the S, As, and P atoms forming part of the acid groups SO_3H, AsO_3H_2, PO_3H_2, and other similar groups do not possess an unshared electron pair, their π-electron systems can be assumed to be isolated and to be virtually uninvolved in conjugation. The influence of such groups can be regarded as a perturbation, which alters the Coulombic integral of the carbon atom adjoining the group, as suggested by Wheland and Pauling.[166] The parameters of the heteroatom necessary for this purpose are calculated by Rasch's method;[167] the overlap integrals are found from tables;[168,169] the ionisation potentials are taken from Vedeneev's handbook,[170] the effective charges are calculated in accordance with Slater's rule,[171] and the interatomic distances are taken from tables.[172] The heteroatoms incorporated in the π-electron system are taken into account by introducing semiempirical parameters for the Coulombic and resonance integrals.[26]

At the present time the task which is to be performed by means of the quantum–chemical theory of the structure and action of OR is fairly limited. In the first place, it is necessary to understand the nature of many of the factors already known, for example the influence of the type of substituents, their positions, etc. Using the data obtained, it is possible to formulate certain hypotheses concerning the alteration of the structure of the given OR, which can lead to the required change in its properties: an increase in the sensitivity, selectivity, and contrast of the reaction, in the stability of the complex, etc. New OR, whose analytical value is then tested in practice, are synthesised on the basis of these postulates.

We shall consider the question of the problems of interest for the study of OR which can be actually solved by the computational methods of the quantum–chemical theory of polyatomic molecules. The most common computational method is the self-consistent field method or the Hartree–Fock–Roothaan method, which can lead to the solution of an extremely large number of problems of practical importance

when account is taken of correlation effects.[26,173,180] In calculations on polyatomic molecules mathematical difficulties arise and investigators are forced to introduce approximations of various kinds and to abandon rigorous versions of the theory in favour of semiempirical ones.[174]

Such methods are even more complex than, for example, the Hückel or the Pariser–Parr–Pople methods and their application requires a large amount of computer time; however, the development of computers makes their large-scale application feasible.

We shall consider certain conclusions which can be reached on the basis of the experience already gained in employing quantum–chemical methods for the solution of various problems associated with the structure and properties of OR. One of the first problems in the theory of OR whose solution by quantum–chemical methods has begun involves the explanation of their colour and the causes of its change on complex formation. One may say that this problem is one of the most important and, moreover, it can be best solved using quantum-chemical methods. The vast majority of OR have an extensive conjugation system and the long-wavelength bands in the spectrum are associated with the $\pi-\pi$ transitions (transitions between states of delocalised electrons)–this makes it possible to employ effectively various methods based on the π-electron approximation. The Pariser–Parr–Pople method, which, when combined with configuration superposition methods, makes it possible to simplify the problem of selecting the parameters and to carry out calculations not only for singlet but also for triplet excited states, is preferable for the calculation of the electronic spectrum.[173] As a result, it is possible to include in the investigation also luminescence spectra, which is an extremely promising feature of the analytical application of OR. The Hückel method is in principle inapplicable for this purpose.

The main difficulty in the calculations of the electronic spectra consists in the fact that, since a semiempirical method is used, it is necessary to select a system of initial parameters which would describe satisfactorily not only the spectrum of the given OR (this is not difficult to do) but would also be capable of being transferred to molecules of a specific class, which would lead to the possibility of predicting the spectroscopic properties of a large group of reagents.

By carrying out the appropriate calculations for both OR and for the complex, it is possible to find a way whereby new reagents can be sought. The construction of schemes relating the positions of the long-wavelength absorption band to the site at which the substituent is introduced in the OR molecule is useful in this connection. Examples of such schemes can be found in the literature.[174]

Using this kind of approach and comparing the wave functions for the highest occupied and lowest unoccupied orbitals of the molecules of isomeric phenolazonaphthols, Pilipenko et al.[175] concluded that the azo-derivatives of 1-naphthol should give rise to a more contrasting reaction than the azo-derivatives of 2-naphthol. The reagents synthesised confirm the above hypothesis. Theoretical analysis also led to the conclusion that the contrast of the reactions can be increased by introducing substituents into the aromatic nuclei of OR molecules and that it is useful to employ substituents which exert only an inductive influence. This led to the synthesis of an OR, namely Picramine Epsilon, whose reaction with zirconium and copper is twice as sensitive as that of Picramine P used for this purpose hitherto.[176]

Quantum–chemical calculations helped to demonstrate the likely usefulness of the synthesis of new OR containing the *oo'*-aminohydroxyazo-group and the *oo'*-carboxyaminoazo-group. These OR proved to be extremely sensitive and selective in reactions with palladium, rhodium, molybdenum, and platinum.[177] *N*-Methylanabasine-α-azo-4-cyclohexylresorcinol has been synthesised on the basis of a preliminary calculation for the photometric determination of indium.[178]

Together with the study of spectroscopic properties, quantum methods have also proved useful for other purposes. They can be used, for example, to study charge transfer in oxidation-reduction reactions. Thus, quantum–chemical studies of the electronic structures of OR as a function of the character of the substituent, resulted in the specific synthesis of new reagents: 4-arsono- and 4-phosphonophenylanthranilic acids, phosphonodiphenylamine, and diphosphonodiphenylamine, which are effective oxidation-reduction reagents for the determination of iron, chromium, and vanadium.[179]

There are as yet few examples of the specific synthesis of OR, but one should note that the number of special quantum–chemical studies whose aim is to predict new reagents is also still very small. The limited number of examples of this kind arises mainly due to the fact that analytical chemists have made little use in their investigations of quantum–chemical computational methods, particularly those where account is taken of all the valence electrons, such as CNDO, INDO, and especially MINDO/3.[180]

Attention must be drawn to the great benefit which theoretical analytical chemistry can derive from the application, together with the usual language of structural formulae, of the language of molecular diagrams based on concepts of fractional atomic charges and fractional orders. Numerous examples have shown that molecular diagrams in many respects promote the elucidation of analytical reactions. It is also significant that such molecular diagrams change comparatively little when more complex methods for their calculation are resorted to.

4. Conformational Analysis

The most important characteristic of OR and their complexes which can be successfully investigated by means of modern theoretical chemistry is the geometry of the systems. The study of geometrical parameters is particularly important, because the cause of complex formation reactions and the spectroscopic properties of complex molecules are in many respects determined by their shape and geometry.

Molecular geometry can be determined by theoretical conformational analysis based on the approximation of atom–atom pair potentials. This method, which has been examined in monographs,[181,182] is used widely to investigate the most varied organic compounds, including large biological systems. In almost all cases where it was possible to compare the results of such conformational calculations with experimental data or with the results obtained via other independent calculations it was found that the method is fairly reliable. This makes it possible to regard it as a procedure with a high predictive power.[183]

The mathematical task reduces to finding the potential energy minimum for the system by varying the interatomic distances. This problem can be solved with the aid of well known mathematical procedures. The simplicity of the expression used for the potential energy makes it possible to formulate the problem formally and to develop special computer programmes distinguished, on the one hand, by great power, and on the other hand, by a great simplicity of the representation of the initial data; this has made the methods of theoretical conformational analysis very accessible.

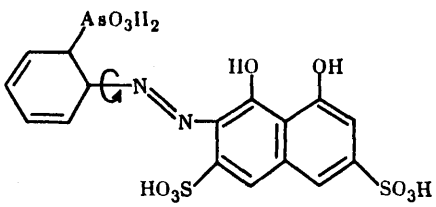
The conformations of a number of organic reagents of the arsenazo III group and related compounds have been calculated[183] and the possibility of rotation about the $C_{Ar}-N$,

N=N, C_{Ar}–AsO_3H_2, C_{Ar}–SO_3H, C_{Ar}–COOH, and C_{Ar}–OH bonds as well as the possibility of the deformation of the valence angles at the nitrogen atoms in the azo-group and the oxygen atom in hydroxy-groups have been examined. Calculations showed that the molecular skeleton of organic reagents without substituents, such as arsenazo III, is planar. The rotation about the C_{Ar}–N bond at the naphthalene nucleus leads to the appearance of stereoisomers differing in the orientation of the azo-group. Regardless of its orientation, all the isomers are energetically equivalent. The substitution of the hydrogen atoms in the 1- and 8-positions in the naphthalene nucleus by hydroxy-groups results in a sharp differentiation of the possible conformers as regards energy: the conformations in which there is a possibility of O–H...N hydrogen bonds are energetically more favourable (approximately by an amount equivalent to the energy of the hydrogen bonds formed) than the conformations in which there are no hydrogen bonds. The formation of conformers containing the O–H...O hydrogen bond (asymmetric conformations) is also possible in principle. All the possible conformations of such molecules are planar.

The presence in a system of this kind of a bulky rotating group results in a sharp increase of the complexity of the picture and renders the principal molecular conformations non-planar. The conformations in which two hydrogen bonds are formed have the lowest energy. At the usual temperatures the equilibrium mixtures can contain only those forms because they are energetically more favourable (the energy gain is 10–20 kcal mol^{-1}).

In order to elucidate the mechanism of the complex formation reaction or to interpret the experimental data for the formation of complexes by azo-reagents with the elements, it is sufficient to know merely the equilibrium geometry of the conformers; it is essential to know how rigid are particular conformations and what is the approximate energy expenditure needed for rotation about the bonds in order to attain the most favourable geometry for the formation of the complex; it is also important to estimate the feasibility of the transition from one conformation to another.

Such calculations for arsenazo I



showed[184] that the rotation about the C_{Ph}–N bond (indicated by an arrow in the schematic diagram above) is fairly free: rotation by ~30° requires an energy expenditure of ~1 kcal mol^{-1}; consequently the OR can readily undergo a change in conformation on complex formation. The barrier to the transition to a neighbouring (relatively unstable) conformation is also low and amounts to 4–5 kcal mol^{-1}.[183,184]

Conformational maps[182] from which one can infer the "softness" or "hardness" of the OR molecule and the energies of the transitions from one conformation to another can also be obtained from the calculations. It was found that, despite the abundance of the possible conformations, as a rule only one conformer is present under the conditions of analytical reactions (we shall not consider here tautomeric transformations and the possibility of the simultaneous presence of several tautomeric forms) and its structure is nearly planar (the deviation of the benzene ring from the plane of the naphthalene ring ranges from 0° to 30° depending on the substituents). The possible conformations of the OR are fairly soft. This means that the same functional group, for example, the *o*-arsonazo-*o'*-hydroxy- or *o*-phosphonoazo-*o'*-hydroxy-group, can satisfy the coordination requirements of many metal cations which can in principle interact with it.

This is one of the most important conclusions reached with the aid of conformational analysis. The selectivity of the reagent can be inferred from its softness or hardness. The OR of the arsenazo I and arsenazo III groups are known to be unselective; they interact with many elements, which in fact was to be expected in view of the softness of the conformations of the reagents of this group.

Similar conformational analysis has not so far been carried out for OR of other groups. If it is confirmed that the softness or hardness of the conformations of the OR is directly related to its selectivity, then conformational analysis of compounds of different classes will possess predictive power and will become one of the methods for the theoretical search for specific selective or group reagents. The knowledge of the geometry of the OR and its complexes is essential also for the subsequent quantum–chemical calculation.

5. Estimation of the Reactivities of Organic Reagents

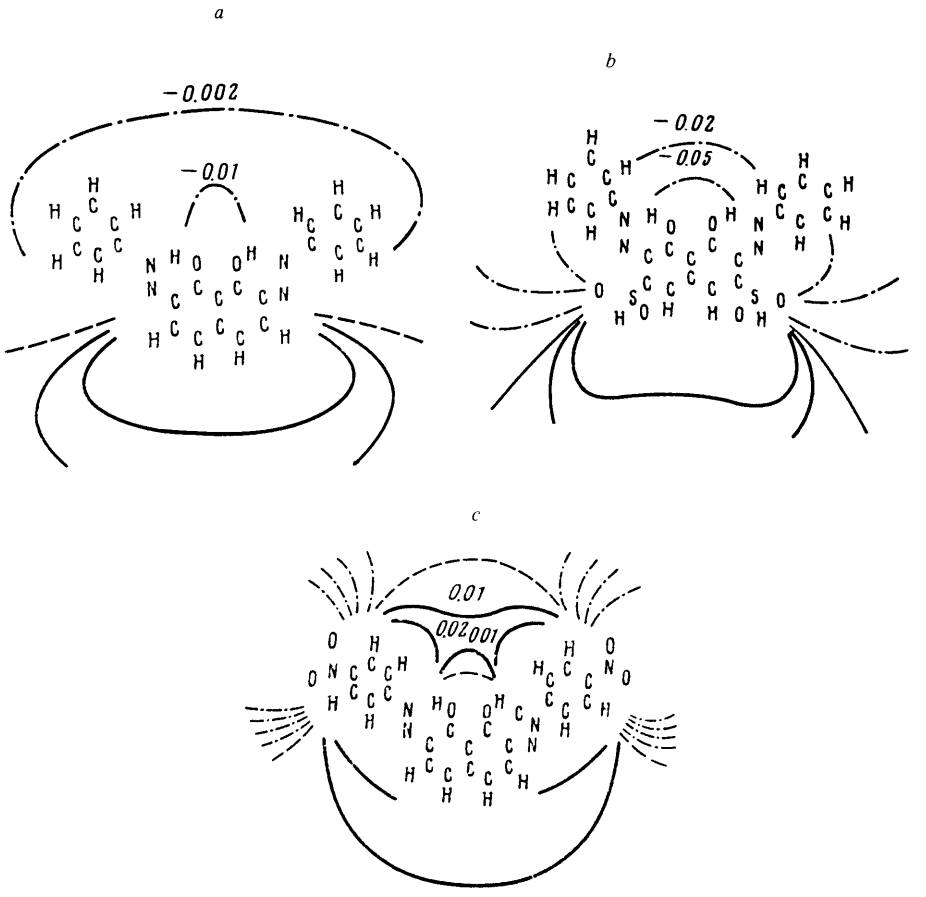
In recent years quantum–chemical methods have been used in the study of the reactivities of OR and of the mechanisms of complex formation reactions. As a rule, the complex formation reaction, especially in its first stage where the metal cation or any other inorganic or organic ion is still comparatively remote from the molecule of the OR, has a distinct electrostatic character. This involves the mutual approach of the charged species and the molecule of the OR, which can be both charged and electrically neutral, but, by virtue of its steric structure and the complex distribution of charges within it, it gives rise to an inhomogeneous electrostatic field along its immediate periphery. The electrostatic field can promote the approach of the metal ion to the reaction centre or conversely can hinder its movement, whereupon the reaction becomes impossible or is retarded. Thus arises the problem of investigating the electrostatic field around the molecule at distances of the order of magnitude equivalent to 2–3 atomic dimensions.

The solution of this problem does not apparently require an especially accurate calculation and the treatment can be restricted to approximations of the type of point charges calculated by the CNDO, INDO, and certain other methods. The methods based on the π-electron approximation are naturally inapplicable in this instance. We shall quote certain model examples demonstrating the dependence of the electrostatic field of the OR molecules on the substituent.

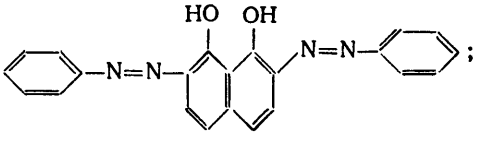
The Figure shows maps of the molecular electrostatic potential calculated for different 2,7-bisazo-substituted 1,8-dihydroxynaphthalenes.[183–185] The distribution of the electrostatic fields in these molecules either facilitates or hinders nucleophilic or electrophilic reactions. In reagents of the group of 2,7-bisazo-substituted chromotropic acid (or 1,8-dihydroxynaphthalene) it is possible to differentiate several functional–analytical groups. We shall consider one of them—the peridihydroxy-group. In the model OR illustrated in Fig.*b* the negative electrostatic potential in the vicinity of the given reaction centre has increased compared with the model reagent in Fig.*a* by a factor of 5 solely as a result of the introduction of two sulpho-groups into the naphthalene nucleus. This model OR is close to a real reagent, namely to a reagent based on chromotropic acid. Naturally the sulpho-groups exert only a weak influence on the distribution of the π-electron density on the atoms incorporated in the conjugation chain of the molecule. This also applies to the

oxygen atoms in the functional–analytical group of the model OR.

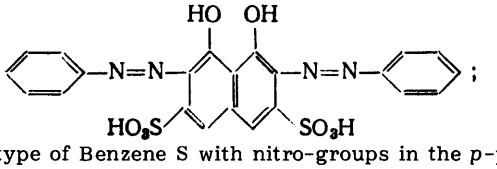
The introduction of nitro-groups in the *p*-positions in the benzene rings of the model OR (Fig.c) reverses the sign of the electrostatic potential. The π-electron density on the atoms forming part of the composition of the functional–analytical group hardly changes under these conditions. At the same time the experimental data show unambiguously a sharp alteration of the reactivity of the OR after the introduction of sulpho-, nitro-, amino-, and other groups even



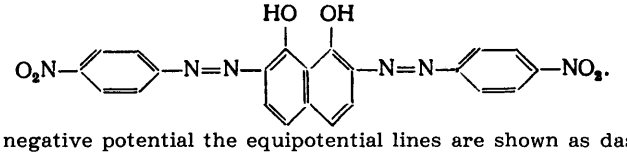
The molecular electrostatic potentials of OR (section in the plane of the molecule): *a*) model reagent of the type of Benzene S without sulpho-groups in the naphthalene nucleus:



b) the Benzene S reagent



c) a model reagent of the type of Benzene S with nitro-groups in the *p*-positions in the benzene rings:



In the region of the negative potential the equipotential lines are shown as dash-dot lines. In the region of the positive potential they are shown as continuous lines; the zero potential lines are indicated by a series of dashes; the numerals denote the potential in e/A^{-1}.

into parts of the molecule remote from the functional–analytical centre. Thus the observed change in the reactivity of the OR can be attributed solely to a change in the molecular electrostatic potential in the immediate (1–3 Å) environment of the functional–analytical centre of the OR.

This comparatively new approach to the theoretical study of the reactivity of the OR can also be used to study their interaction with metal cations to form chelate compounds. The initial structures of the reactants (the structures of the reagents and of the form of the metal under the given conditions) and the structure of the final reaction products have so far been investigated by different procedures; the possible structures of the reaction intermediates have sometimes been discussed. Maps of the molecular electrostatic potentials of the reagents make it possible to follow to some extent the pathway (more precisely the likely site of attack) traversed by the metal ion towards the OR molecule. This may make it possible to specify more precisely the structure of the complex in those cases where there are several sites at which the metal ion can be attached in principle. One cannot rule out the possibility that the selectivity of the OR, the rates of its reactions, and its other analytical characteristics depend to some extent also on the distribution of the molecular electrostatic potential.[185]

In conclusion of the brief survey of the applications of the quantum–chemical methods in the solution of the problems of the theory of the action of OR, we may note that the use of quantum–chemical research techniques has not introduced radical changes into the principal postulates of the theory of the action of OR. On the other hand, during the first decade after the introduction of these methods into the working arsenal of analytical chemistry, it has been convincingly demonstrated with their aid that the theoretical ideas constructed on the basis of traditional research techniques are correct. In the same stage quantum–chemical methods made it possible to obtain much new information about the structure of OR which might have been obtained, albeit with much difficulty, also by means of traditional methods.

The second, modern stage in the application of quantum–chemical methods in analytical chemistry (which began approximately in 1970) is characterised by the possibility of obtaining new information (detailed characteristics of the electronic structures of OR, their electrostatic potential fields, and their reactivities), which cannot be obtained in principle by traditional methods. One can also imagine a transition in the immediate future to a third stage, which will make it possible to predict specific syntheses of OR with specified properties.

6. Kinetics of Colour Reactions

The study of the rates of rapid chemical reactions is important both for the theoretical and practical aspects of analytical chemistry. Certain chemical reactions, which have been regarded for a long time as rapid, are retarded so much under certain conditions that this can introduce significant errors into chemical analysis. It is important to take into account the retardation of the reaction in the development of automatic schemes for the continuous control of industrial processes, for example, in analysis in a stream of liquid. Hitherto few studies have been made on new practical possibilities for increasing sensitivity and selectivity which might be realised if it were possible to employ as analytical forms the reaction intermediates whose principal spectroscopic characteristics can be measured either with the aid of high-speed spectrophotometers or by the application of external influences which arrest or retard the reaction at a specific stage.

However, the mechanisms of the majority of the chemical reactions of analytical importance still remain unelucidated. Even if the composition and structure of the initial reactants and of the analytical product are known, as a rule nothing is known about the structure of the intermediates produced in the interaction of the cation of the given element with an OR having a fairly complex structure.

Until recently, colour reactions were divided into slow and "instantaneous". The kinetics of the latter reactions were hardly investigated, although the rapid reactions might have been in fact of greatest interest for the understanding of the process mechanism because in such cases the mechanism of the formation of complexes operates in a pure form (slow reactions are usually complicated by the hydrolytic process, by the dehydration of metal ions and OR molecules, and other side reactions).

The advances in the study of rapid reactions achieved in related fields of chemistry stimulated the application of the newly developed methods also to the study of analytical colour reactions. Procedures have appeared in recent years for the investigation of the reaction kinetics which make it possible to investigate reactions with a half-reaction time ($t_{1/2}$) ranging from 10^9 to 10 s.[186] It was established in almost all cases that colour reactions are not simple single-stage reactions but proceed with formation of at least one or several intermediates. The study of the reactions of aluminium with Xylenol Orange and Aluminocrezone[187] established that the former reaction proceeds in accordance with a kinetic second-order equation and the latter in accordance with a first-order equation.

In the study of the complex formation reaction between gallium and Methylthymol Blue[188] the formation of the intermediate $Ga(OR)_2$ in the course of the formation of the final complex GaOR was established. It was shown that the process is of first order with respect to both the metal and the OR. Its rate-limiting stage involves the interaction of the complex $Ga(OR)_2$ with the $Ga(H_2O)_n$ cation. The same reagent enters into a first-order reaction with nickel[189] and lanthanium.[190] The slow reaction of arsenazo III with zirconium has also been investigated.[191]

In the case of rapid reactions, the kinetic spectrometric method is very useful in the analysis of a mixture of substances involving complex reactions but differing as regards the formation or decomposition of the complexes. The flow version of the method has been used for the analysis of alkaline earth and certain transition elements.[192] The kinetic method for the quantitative determination of individual lanthanides in the presence of other lanthanides employs the reaction of complexone III (EDTA) with the coloured complexes formed by the lanthanides with Xylenol Orange, it proceeds in accordance with the following scheme:

$$LnX + EDTA \rightleftarrows LnEDTA + X,$$

where Ln is the lanthanide ion, X is the anion of Xylenol Orange, and EDTA represents ethylenediaminetetraacetic acid. In relation to the coloured complex LnX, the above reaction is of first order; in the series of lanthanides the rate of attainment of 50% reaction varies from 236 s^{-1} to 30 s^{-1}.[193] The method developed makes it possible to determine certain lanthanide elements in the presence of a tenfold excess of other lanthanides.

The reaction of UO_2^{2+} with arsenazo III, widely used in analytical chemistry, has also been investigated by spectroscopic-kinetic methods.[144,194] The absorption was measured on a specially designed spectrophotometer with electronic scanning of the spectrum, which ensures the recording of optical absorption spectra in the range 230–800 nm and also the recording of kinetic curves at any wavelength. Analysis of the absorption spectra and of the kinetic curves obtained under different

conditions (concentration, pH of the medium, the presence of other substances in solution, temperature, etc.) permits definite conclusions about the mechanism of the complex formation. It was found that the order of the reaction of UO_2^{2+} with arsenazo III is close to unity; the rate of reaction is proportional to the concentration of one of the components; the determining factor is the concentration of the active, ionised form of the OR. This means that, although the direct interaction of the uranyl ion with the undissociated form of the OR cannot be ruled out, the main process, which determines the rate of reaction, is the interaction of the uranyl ion with the active and especially the dissociated form of the OR.

More complete information about the mechanism of a complex colour reaction can be derived from the study of the absorption spectra of the reaction products recorded by the given apparatus in the course of the reaction. This makes it possible to follow the variation of the concentrations of the individual substances involved in the reaction, i.e. one can obtain their kinetic curves and one can calculate the rate constant for each elementary stage. The constants obtained in this way then have an entirely concrete significance and are not conventional (overall). It is fairly difficult to carry out such an experiment, since it requires, in particular, a high accuracy of the measurements and the ability to resolve unambiguously the complex spectral curves into simple components and also the ability to choose the optimum reaction conditions which will ensure that the reaction proceeds via an unambiguous mechanism. It is likewise essential to have at ones disposal a clear-cut scheme for the interpretation of the results.[184,185]

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Some information about the state and prospects for the development of a branch of science can be obtained by a numerical scientific study of publications. The number of communications devoted to the investigation and general analytical employment of OR varies according to different data from 600 to 1300 per annum, while the annual number of publications on the analytical chemistry of inorganic substances is of the order of 4300–4700.[196,197] The available literature data[198] have shown that different branches of analytical chemistry have undergone one of three types of evolution at different times: regression, saturation, or growth. According to statistical data, studies in the field of OR have not yet reached the stage of saturation and are in the growth stage. The fraction of publications on OR constitutes, according to some data,[197] about 30% of the total number of communications on analytical chemistry.

The main bulk of the applications of OR are in photometry. Photometric analysis is one of the commonest methods. The publications on the photometry constitute ~30–35% of all the publications devoted to analytical chemistry.[199,200] More than half of all the analyses in industry, in agriculture, in medicine, and in the monitoring of the pollution of the environment are performed by spectrophotometric methods. There is reason to believe that in the immediate future (20–30 years) spectrophotometry will become the most important method of chemical analysis. This is indicated by the new ideas and developments in the field of the automation of analysis and analytical apparatus (the flow-injection system and chemical sensors) and also by the advances in the synthesis of new OR.

The synthesis of new highly effective OR is at the present time largely determined by the level of development of the theory of the action of such reagents. This is associated with the fact that the semiempirical search, which has been hitherto the main basis for the creation of new OR, has been virtually exhausted. Theoretical ideas already exist which make it possible to synthesise structural analogues of the known reagents by introducing functional-analytical and other groups or by slight modification of the main carbon skeleton of the molecule of the prototype reagent. This is a reliable way of altering and improving the properties of OR. However, the expected and subsequently observed effects, although satisfactory and sometimes considerable, are not fundamental in the sense that they make it possible to obtain OR specific to some chemical element or to achieve a sharp increase, for example, by an order of magnitude, in the sensitivity of the reaction.

A characteristic feature of the theoretical developments in the last 10–15 years, associated with the application of quantum-chemical and other theoretical research techniques, consists in the search for specific syntheses of new classes and groups of OR with properties specified beforehand. There is reason to believe that this procedure will lead to the creation of new and highly effective OR.

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