U. D. C. 547.556.7

The Current State of the Problem of the Structure and Reactivity of Aromatic Diazo-compounds

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The author, one of the leading investigators of the chemistry of diazo-compounds, describes in this article his views on the structure and reactivity of aromatic diazo-compounds. In the usual sense of the of the word, this is not a complete review of studies on diazo-compounds; it does not reflect all the numerous data published recently and does not contain a critical analysis of new results obtained in the last decade. The review describes the author's views based on the experimental data from his laboratory. The bibliography comprises 32 references.

The Editors

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1. THE DIAZOTISATION REACTION

The study of the detailed structure of aromatic diazo-compounds is at present impossible without establishing the relations governing their formation. Therefore, before considering the structure, it is necessary to describe at least briefly the modern views on the preparation of aromatic diazo-compounds.

Without exaggeration one can say that the diazotisation reaction, as well as the structure of the diazo-compounds formed, is one of the most interesting and at the same time the most complex problems of organic chemistry. The experimental difficulty consists in the extreme instability and variability of diazo-compounds, which makes it difficult to isolate the individual substances.

The simplest and the most widely used method for diazotisation consists in treating the amine dissolved in an aqueous inorganic acid, with alkali metal nitrites. An acid medium during the diazotisation reaction is essential, on the one hand in order to prevent the shift of the ammonium ion $\rightleftharpoons$ amine equilibrium to the right (although, as we shall see below, the free amine is in fact diazotised and not its salt), which makes the amine insoluble, and, on the other hand in order to form the most active species participating in the reaction with the amine during its diazotisation. Finally a distinctly acid medium in the diazotisation process prevents the formation of certain side products.

Alkali metal nitrites are used in strictly stoichiometric amounts. An excess as well as a deficiency have an unfavourable effect on the stability of the diazo-compound formed. With decrease of the basicity of the amine diazotised, it is difficult to carry out the reaction in dilute aqueous solutions. In such cases concentrated acids (usually sulphuric) are used as solvents together with dry alkali metal nitrites[1]. Apart from these main diazotisation methods, there exist also certain others, the discussion of which would not throw any fundamentally new light on the problem.

The occurrence of the diazotisation reaction in an acid medium is as it were evidence that not the free amine but the salt is diazotised. However, if we remember that in a fairly concentrated acid there is always an equilibrium between the arylammonium ion and the free amine base and also that aromatic amines are fairly weak bases, the hypothesis that even in a strong acid medium the free amine is converted into the nitroso-derivative is not unexpected. Various workers arrived at this conclusion independently[2-6] and its validity was proved in 1958 by Hughes et al using kinetic methods[7]. However. recently publications have appeared where the possibility of diazotisation of certain arylammonium salts, probably by a synchronous mechanism, is postulated[8]. In either case, the first stage in the diazotisation process is the introduction of a nitroso-group into the amino-group. In principle, this reaction does not differ from the nitrosation of secondary aliphatic aromatic amines and is one of the amine acylation reactions.

In accordance with the electrophilic mechanism of the substitution of a hydrogen atom in acylation, it was to be expected that the nitrosating species would carry a positive charge or would exhibit a strong tendency to acquire such a charge.

The nitrous acid formed in the first instant of the reaction between alkali metal nitrites and the inorganic acid also reacts with the inorganic acid, giving rise to a number of equilibria which can be represented as follows:

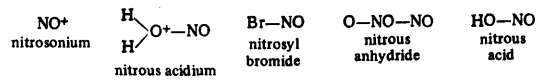
$$HNO_2 \overset{H^+}{\rightleftarrows} H_2NO_2^+ \begin{cases} \xrightarrow{NO_2^-} N_2O_3 + H_2O \\ \longrightarrow NO^+ + H_2O \end{cases},$$

and in the presence of hydrogen halides:

$$HNO_2 \rightleftarrows H_2NO_2^+ \overset{Hal^-}{\rightleftharpoons} HalNO + H_2O.$$

These mechanisms show that in sulphuric acid a powerful nitrosating species is formed and readily gives rise to the nitrosonium cation, which is the essential electrophilic agent. In the presence of hydrogen halides nitrosyl halide with a highly polarised nitrogen–oxygen bond is formed, which also leads to the presence in the medium of an electrophilic species. Bearing in mind the above equilibria in the nitrous acid–inorganic acid system, all

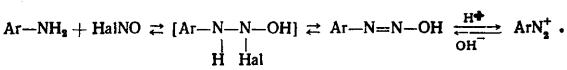
possible nitrosating agents can be arranged in the following sequence with respect to their effectiveness:



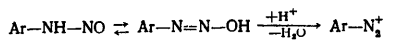
Nitrosyl halide HalN=O, which adjoins nitrous acidium as regards its activity but is formed only in hydrogen halide solutions, stands somewhat in isolation in the above series. Experimental proof of the validity of this sequence of nitrosating species in terms of their activity was found by Hammett, Ingold, and others[9,10].

It appeared that the interaction of the nitrosonium ion with the free base of an aromatic amine should give rise to a nitrosammonium ion. Therefore the nitrosamine should be at least slightly basic. In one of the present author's studies[11] it was shown that the basic properties of nitrosamine are extremely weak. Thus even if the nitrosammonium ion is formed (this is the view of, for example, Zollinger[12]), it must be rapidly hydrolysed under the reaction conditions. Consequently its formation should be regarded as a quasi-steady-state intermediate reaction stage. Another mechanism of the nitrosation reaction, in which the interaction of the nitrosonium ion with the amine and the elimination of a proton take place synchronously, is extremely probable. The difference between the both mechanisms is minimal.

In diazotisation in hydrogen halide solutions the first reaction product is a complex formed by the addition of the amine to nitrosyl halide, which is subsequently converted into a diazonium salt:



The conversion of nitrosamine into a diazonium salt is fairly clear in broad outline. Since the nitrosamine is in tautomeric equilibrium with the amphoteric diazohydroxide, in an acid medium the latter reacts instantaneously with the inorganic acid and is converted into the diazonium salt:



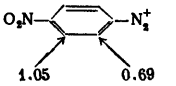
2. THE STRUCTURE AND REACTIVITY OF DIAZO-COMPOUNDS

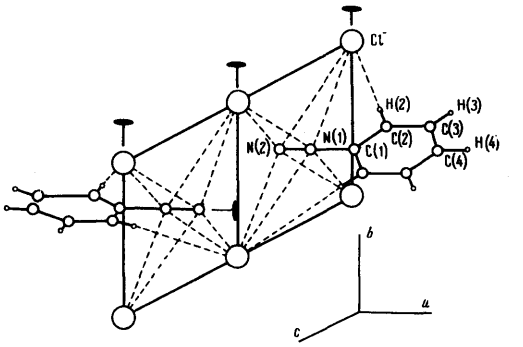
X-Ray diffraction analysis of diazonium salt crystals showed[13] that the anion is at a distance of 3.5 Å from the diazonium group and slightly closer to the extreme nitrogen atom. This is evidence that both nitrogen atoms have positive charges, which is extremely important for the understanding of the structure and reactivity of the diazonium cation.

The effective radii of the anion and the nitrogen atoms overlap, albeit to only a slight extent, but probably enough for the bond between the anion and cation to vary somewhat in type, while remaining ionic, depending on the properties of the anion. This is probably the cause of the differences between the properties of various salts of the same diazonium cation.

The above X-ray diffraction analysis shows that the diazonium cation is a planar system with nitrogen atoms linearly distributed in the plane of the aromatic ring; the the nitrogen atoms are thus *sp*-hybridised. The anion is located on one side of the plane of the organic ion. The Figure gives a clear representation of the steric structure of benzenediazonium chloride.

As a substituent of the aromatic ring, the diazonium group is strongly electronegative. Its electronegativity is approximately twice as pronounced as that of the nitro-group[14-16], which means that, in relation to the diazonium group, the aromatic ring is an electron donor even when it includes an electron-accepting substituent such as the nitro-group. This is demonstrated by the degrees of electron shielding characterising the depletion of the electron cloud and determined by NMR method, resulting from the electron-withdrawing effect of the nitro- and diazonium groups in the *para*-positions relative to one another: they are 1.05 and 0.69. This can be illustrated by the following scheme:





Schematic representation of a benzenediazonium chloride crystal according to X-ray diffraction data.

In the unsubstituted benzene ring the above numbers are 2.72.

It has been firmly established that the bond between the nitrogen atoms approaches the triple bond type[17,18]. This is illustrated in the Table, where the first column lists the substituents in the phenyldiazonium ring and the remaining columns give the absorption frequencies of the triple bond in liquid paraffin and in water together with the multiplicities of the bond between the nitrogen atoms.

It is clear from the Table that the bond multiplicity varies between 2.645 and 2.850. Calculation of electron density by the MO method in the Hückel approximation carried out by Schuster and Polansky[19,20] led to similar conclusions. The triple bond character of the link between the nitrogen atoms contradicts to some extent the X-ray diffraction data, according to which a greater part of the positive charge is concentrated on the outer nitrogen atom, since a triple bond implies the presence of only one positively charged nitrogen atom (linked directly to the ring).

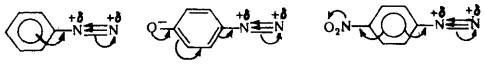
The following considerations may be adduced to eliminate these conditions. Of the three bonds between the *sp*-hybridised nitrogen atoms only one π bond, the plane of the electronic vibrations of which coincides with the π-electron plane of the aromatic ring, is capable of transmitting conjugation. As a result of the presence of

this bond, the aromatic ring is conjugated with all its substituents and the extreme nitrogen atom. Infrared spectroscopic data show that this conuugation may influence to some extent the link between the two nitrogen atoms causing its approach to or departure from the "pure" triple bond.

Frequencies and multiplicities of the nitrogen–nitrogen bonds in various benzenediazonium compounds.

Substituent	In liquid paraffin		In water	
	ν	P	ν	P
p-NO_2	2304	2.850	insol.	—
m-NO_2	2302	2.847	ditto	—
p-SO_2NH_2	2290	2.830	2296	2.837
p-$COOCH_3$	2299	2.843	2292	2.834
m-Cl	2306	2.853	insol.	—
m-$COOCH_3$	2298	2.841	2290	2.830
p-$COOC_2H_5$	2300	2.845	2288	2.827
p-SO_3^-	2284	2.821	2286	2.824
m-SO_3^-	2284	2.821	2288	2.827
p-I	2282	2.818	2278	2.812
p-Br	2286	2.824	2280	2.815
p-Cl	2290	2.830	2282	2.813
p-F	2294	2.836	2288	2.826
m-OCH_3	2298	2.841	decomp.	—
H	2296	2.837	2284	2.821
m-CH_3	2296	2.837	decomp.	—
p-CH_3	2286	2.824	2276	2.809
p-OCH_3	2252	2.773	2250	2.771
p-$NHCOCH_3$	2252	2.773	2252	2.773
p-OH	2242	2.756	2236	2.750
p-NH_2	2183	2.673	—	—
p-$N(CH_3)_2$	2166	2.649	2164	2.645

The second π bond, which is not in the plane of the π-electron cloud over the aromatic ring, and the third σ bond can transmit only the inductive effect of the positively charged nitrogen atom to the extreme nitrogen atom, which also carries in consequence a permanent positive charge, this being confirmed by X-ray diffraction data. It appears that the following formulae of the most typical diazonium cations reflect to some extent all that has been said about their structure:



The Reactivity of Diazonium Salts

The most important reaction of which aromatic diazo-compounds are capable is azo-coupling. Therefore, when speaking of the reactivity of diazo-compounds, one usually has in mind their reactivity in the azo-coupling reaction. Since various investigators have established rigorously that only the diazonium cation enters into the azo-coupling reaction, the reactivity in this reaction is usually attributed to the diazonium cation.

Since within the framework of a short article it is impossible to consider all the reactions of which aromatic diazo-compounds are capable, here too only the azo-coupling reaction, interpreted, however, in a somewhat extended sense, will be dealt with.

From the above considerations, it follows inevitably that the reactivity of the diazonium cation is linked to the electrophilic properties of the extreme nitrogen atom or, in a more restricted sense, the Lewis acid strength of the diazonium cation.

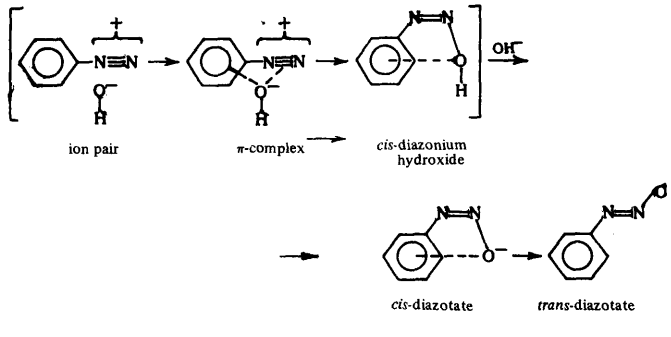
Bearing in mind that the aromatic ring with any of the usual substituents is always an electron donor in relation to the diazonium group and therefore always neutralises to a greater or lesser extent the positive charge of the extreme nitrogen atom, the problem of the reactivity reduces to the degree of neutralisation of the charge by various substituents. From this point of view, p-nitrobenzene diazonium for example, should be much more reactive than p-dimethylaminobenzenediazonium.

At the same time the first of the above substances is a stronger Lewis acid than the second. Evidently the strength of the Lewis acid and its reactivity in the azo-coupling reaction should be correlated, since acidity constitutes a special case of electrophilicity. Therefore the reactivity of the diazonium cation is initially most conveniently investigated in its reaction with a hydroxide ion. As will be shown below, despite its apparent simplicity, this reaction has certain features which permit it to be treated as a model for more complex cases.

The reaction between a hydroxide ion and a diazonium cation begins with the formation of an ion pair. The ion pair should be fairly stable, since the hydroxide ion is oriented by the π-electron system of the aromatic ring and the diazonium group. The gradual conversion of this ion pair into a π complex takes place in such a way that the bond between the hydroxyl and the π-electron system of the ring is maintained, which predetermines the steric configuration of the diazohydroxide formed subsequently. In the π complex the nitrogen atom linked to the ring is in a state of sp-hybridisation and therefore the structure of this complex is still linear.

In the next, slowest reaction stage the π complex is converted into diazohydroxide in which both nitrogen atoms are now in a state of sp^2-hybridisation as a result of which the molecule becomes bent. Since the hydroxyl probably remains linked to the aromatic ring, both residues must occupy *cis*-positions in relation to the double bond of diazohydroxide. Suhr and coworkers[21] found on the basis of a study of PMR spectra of aromatic diazotates that not all the ring hydrogen atoms are equivalent. From this, he concluded that there is a bond between the oxygen of the diazotate ion and the carbon atom in the *ortho*-position, which is also evidence in favour of the *cis*-configuration.

The reaction of the diazonium cation with the hydroxide ion is shown schematically below:



Usually diazohydroxide is not regarded as the final reaction product, since no representative of this series has so far been isolated. It is regarded either as "an intermediate product in a quasi-steady state" or as a σ complex. The present author believes it more logical to

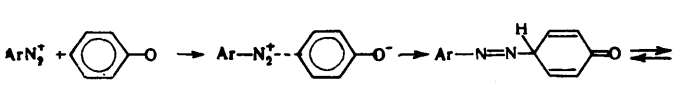
regard the *cis*-(or *syn*-) diazohydroxide as the final compound which has, however, unusual properties enabling it to undergo further reactions under the given conditions. One of the most important properties of diazohydroxide is its amphoteric nature which leads to its rapid acid or base ionisation. The diazotate ion in which the multiplicity of the bond between the nitrogen atoms is 1.4 according to calculations[22], formed on acid ionisation of diazohydroxide, is also capable of *cis–trans* isomerism and in an alkaline medium comparatively readily undergoes a stereochemical transformation, forming the *trans*-(*anti*-) isomer, which is extremely stable.

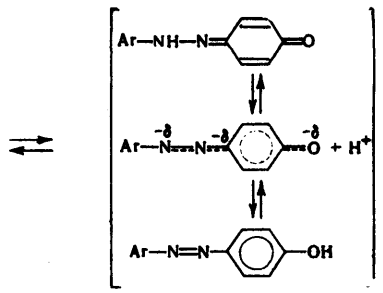
However, the reactions which follow the formation of the *cis*-diazohydroxide should not be included, according to the present author, with the nucleophilic attack proper by the hydroxide ion on the diazonium cation.

Thus one may assume that the reaction between the diazonium cation and the hydroxide anion has an S_N2 mechanism. The substrate (diazonium cation) undergoes the most pronounced changes in this process: the state of hybridisation of the nitrogen atoms changes, the previously non-existent capacity for stereoisomerism appears, etc. It is scarcely possible to regard the hydroxide anion as the substrate in this reaction and the diazonium cation as the reagent. It would then be necessary to assume that the hydrogen atom in the hydroxide ion is substituted. The azo-coupling reaction, which takes place in exactly the same way, is then assumed to have an S_E2 mechanism with a quasi-steady-state intermediate stage. The diazonium cation is regarded as an electrophilic reagent, similar, for example, to the nitronium cation, the chlorine cation, the carbonium cation, and other positive species. "The quasi-steady-state intermediate product" (or σ complex) differs from the final compound by the position of the proton, which is removed from the molecule by any base present in the medium during the second, faster reaction stage.

The present author believes that there is no fundamental difference between the interaction of the diazonium cation with the hydroxide anion and with the azo-component. In both cases the diazonium cation undergoes the same, much more significant changes than the reagent—the hydroxide anion or the azo-component. Also in both cases a covalent bond is formed between the extreme nitrogen atom and the atom of the attacking species. In the first case this atom is the oxygen of the hydroxide anion and consequently one may speak of the acidity of the diazonium cation. In the second case it is a carbon atom, the electrophilic properties of which may be assessed.

On the other hand, analysis of the structure of the so called σ complex ("the quasi-steady-state intermediate product"), formed in the azo-coupling reaction shows that it is none other than the final product in one of its possible tautomeric forms. Its further conversion into another tautomeric form, the azo- or quinohydrazo-form, usually does occur but under certain conditions may not. Therefore in the scheme representing the stages in the azo-coupling reaction—the ion pair, the complex, and one of the possible steric isomers of the azo-compound—the stage in which the tautomer formed is converted into another form, which may involve the inversion of the configuration, is separate from the azo-coupling reaction proper:





Indirect confirmation of the validity of the separation of further reactions of the product from the azo-coupling reaction proper is provided by the wide variety of views concerning the presence or absence of a kinetic isotope effect in the azo-doupling reaction[23]. In some cases it is absent, while in others it is observed. This is probably associated with the different rates of tautomeric transformations of the so called σ complex. The changes in the hybridisation of the carbon atom linked to the extreme nitrogen atom of the diazonium cation are of the usual type accompanying any tautomeric transformation.

Thus it is possible to postulate that the azo-coupling reaction also has an S_N2 mechanism, i.e. the reagent (the azo-component) adds to the triple bond of the substrate (the diazonium cation).

This new approach to the azo-coupling reaction will make it possible to treat from the same standpoint reactions which are at first sight quite different and to combine them in a single system.

The present author has in mind (apart from the azo-coupling proper) the reactions of the diazonium cation with amines leading to the formation of diazoamino-compounds, with alcohols leading to ethers, and with nucleophilic reagents such as the sulphite ion, the nitrilium ion, etc. — in other words all the reactions of the diazonium cation resulting in the formation of a covalent bond between the terminal nitrogen atom and any other atom in a nucleophilic species (base). There is a possibility now of determining the causes of the stereoisomerism, the reactivities of various nucleophilic agents, etc.

It must be emphasised yet again that the properties of the product of the addition of the nucleophilic agent to the triple bond determine its subsequent fate. If this is a product resulting from the attack by an azo-component, then, as stated above, it may undergo tautomeric transformations; if it is a result of reaction with amines, there is a possibility of a rearrangement of the diazoamino-compound formed into an aminoazo-compound; if it is a product of the addition of a hydroxide ion, it undergoes acid ionisation with further stereochemical transformations; if it is a product of the reaction of hydrocyanic acid with the diazonium cation, it undergoes only stereochemical changes; finally, if it is a compound formed as a result of nucleophilic attack on the diazonium cation by any alkoxide, the reaction terminates at this point, etc.

It is interesting to note that in all these cases the sequence of cations arranged in order of increasing or decreasing reactivity is maintained. It is possible to estimate the reactivities of various nucleophilic agents as a function of their structure, and the possibility of further reactions of the primary product of addition to the triple bond.

The capacity of certain diazo-compounds for decomposition on irradiation with ultraviolet light is widely used in engineering. Diazo-compounds with electron-donating

hydroxy-, dialkylamino-, arylamino-, sulphide, etc. groups in the *para*- or *ortho*-positions in relation to the diazonium-group are particularly light sensitive. As a result of the presence of these groups, the neutralisation of the positive charge of the extreme nitrogen atom is considerable. However, infrared spectrophotometric data and calculations by the molecular orbital method in the Hückel approximation suggest that the bond between the nitrogen atoms is much closer to a triple than to a double bond. This is true also in those cases where the *para*- (or *ortho*-) position in relation to the diazonium group contains a readily ionisable hydroxy- or acid imino-group. Therefore the "quinodiazide" structure proposed for these compounds, like the name itself, is hardly accurate. The "quinodiazide" formula must be regarded only as one of the extreme resonance structures, invariably associated with another formula, whereby these substances are represented as inner salts and which makes a much greater contribution.

In accordance with the above considerations, the electrophilic reactivity of diazonium salts with powerful electron-donating substituents in the *para*-(or *ortho*)-position in relation to the diazonium group is reduced, although they, including the so called "quinodiazides", retain their capacity for azo-coupling. On the other hand, their light sensitivity and thermal stability are enhanced[24-26]. The latter is important for applications in engineering.

3. DIAZOHYDROXIDES AND NITROSAMINES

When diazonium salts are treated with alkalis one might expect that the neutralisation of one equivalent of acid would convert the substance into diazohydroxide (as shown above, *syn*-diazohydroxide). However, because of the amphoteric properties of diazonium hydroxide and the high rate of its reaction with the second equivalent of hydroxide ions leading to the formation of the final product (*syn*-diazotate), diazohydroxide is not formed. As shown by Bryuske[27], the theoretical explanation of this is that in an aqueous medium the diazohydroxide is fully ionised. Therefore the attempt to isolate representatives of this class of compound were in vain. The interaction of alkali with diazonium salts leads to the formation of a mixture of diazonium cations and diazotate anions and not diazohydroxide. The amphoteric properties of the latter and the fact that the reaction with the second equivalent of hydroxide ions is faster than with the first constitutes the foundations of all modern hypotheses concerning the structure of aromatic diazo-compounds. These properties of diazohydroxides suggest that, if they are ever isolated, it will be from non-aqueous solutions and even then under non-equilibrium conditions. However, there is no doubt about the existence of diazohydroxides as a necessary logical and chemical stage in the neutralisation of diazonium cations by alkalis. The well known curves obtained by the potentiometric titration of various diazonium cations with alkalis confirm this[28]. As regards *anti*-diazohydroxides, we may note that this structure has been sometimes attributed to the product of the acidification of *anti*-diazotates. However, in a recent study Eiges[29] showed by infrared spectrophotometry, dipole moment measurements, and molecular orbital calculations that in those cases where the product of the acidification of the *anti*-diazotate can be isolated from solutions (and this has been achieved for diazo-compounds with electron-accepting groups in the *para*-position with respect to the diazo-group) it has the structure of a primary nitrosamine. At one time Hantzsch suggested that the nitrosamine and *anti*-diazohydroxide are in equilibrium. This view should evidently be accepted but in a modern sense: the two compounds are in tautomeric equilibrium and the *anti*-diazohydroxide does not exist in aqueous solutions because of its amphoteric properties.

4. DIAZOTATES

Syn- (or *cis*-) diazotates, obtained by the interaction of alkalis with diazonium salts, can be isolated as precipitates, although this operation requires a considerable skill of the experimenter. On heating in concentrated alkalis, these diazotates are converted into stable readily isolated *anti*-(*trans*-)diazotates, which, in contrast to *syn*-isomers capable of undergoing instantaneous coupling with the azo-component, are capable of this reaction only after relatively prolonged treatment with inorganic acids. It will be seen later that this is because the equilibrium in aqueous solutions between the *syn*-diazotate and the diazonium cation is established instantaneously, while that between the *anti*-diazotate and the diazonium cation is attained slowly. There is at present no doubt that both diazotates are stereoisomers. However, it must be emphasised that the modern view differs somewhat from the Hantzsch hypothesis which postulates the stereoisomerism of covalent diazo-compounds (for example, diazohydroxides assuming them to be unionised), while modern chemists postulate the stereoisomerism of the ions (diazotates).

The present author and Shaburov[30] not only succeeded in demonstrating this but also showed the presence of the *syn*-diazotate in solution for the *p*-nitrobenzenediazo-compound, the existence of the *syn*-diazotate of which had not been proved previously. The converse transition of the *anti*-diazotate into the *syn*-diazotate has been demonstated in only a few cases. It occurs when the *anti*-diazotate is irradiated with solar ultraviolet light.

5. EQUILIBRIUM BETWEEN DIFFERENT FORMS OF DIAZO-COMPOUNDS

Various forms of diazo-compounds were mentioned above. We have seen that these include diazonium salts, diazohydroxides, nitrosamines, and diazotates. A mechanism for the interconversions of these forms of diazo-compounds was put forward for the first time by Hantzsch but this now requires some modernisation, revision, and correction. All the forms are present in equilibrium in aqueous solution. The position of this equilibrium depends on the pH of the medium and in some cases may be displaced to a limit where a particular form of the diazo-compound can be isolated and investigated in detail. There are protolytic and tautomeric equilibria. The stereoisomeric transformations do not give rise to equilibria and are rarely reversible.

We shall first attempt to examine special equilibrium systems, included in the general reaction mechanism; purely protolytic equilibria will be artificially separated from tautomeric and stereochemical transformations.

The behaviour of the diazonium cation is typical for dibasic Lewis acid. When acted upon by alkali, it reacts in succession first with one and then with another hydroxide ion and is converted into a diazotate anion. To some extent this occurs also in the absence of alkali: one can then speak of the hydrolysis of the Lewis acid. This acid–base equilibrium has been well investigated. It is established extremely rapidly and has many characteristic features.

The first stage in the interaction of the diazonium cation with the hydroxide ion is, as stated above, the formation of a covalent *cis*-diazohydroxide, while the second, faster stage is the ionisation of the diazohydroxide and the formation of *cis*-(*syn*-) diazotate:

$$Ar{-}N_2^+ \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Ar{-}N{=}N{-}OH \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Ar{-}N{=}N{-}O^-(syn).$$

The neutralisation curves obtained by potentiometric titration do not show a jump in potential after the addition of the first equivalent of alkali as happens in the titration of the usual dibasic acids. This form of neutralisation curve implies that the equilibrium constant for the first reaction stage is much lower than for the second stage[31]:

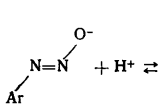
$$K_1 = \frac{[Ar{-}N_2OH][H^+]}{[Ar{-}N_2^+]}; \quad K_2 = \frac{[Ar{-}N_2O^-][H^+]}{[Ar{-}N_2OH]}; \quad K_2 \gg K_1.$$

The condition $K_2 \gg K_1$ means that, when exactly one equivalent of alkali is added to the solution of the diazonium salt, the product is not diazohydroxide as indicated in the above equation, but a 1 : 1 mixture of diazotate anions and diazonium cations. Thus a kind of salt—diazonium diazotate—is formed. This interesting phenomenon is based on the amphoteric properties of diazohydroxide mentioned above. The high rate of equilibration between the diazonium cation and *syn*-diazotate, to which Littler first drew attention[32], gives rise to the apparent capacity of the diazotate for azo-coupling. After a time, the *syn*-diazotate rearranges to the *anti*-isomer under the action of alkalis or heat. Since the basicity of the *anti*-diazotate is lower, this rearrangement involves a spontaneous decrease of the pH of the medium. The stronger is the Lewis acid (diazonium cation) from which the *syn*-diazotate has been obtained the easier is the stereoisomeric rearrangement.

The rearrangement of the diazo-compound from *p*-nitroaniline is so fast that the intermediate formation of the *syn*-diazotate can be observed only by special methods[30]. On the other hand, the more basic the amine from which the diazo-compound has been prepared the more severe conditions are required for the rearrangement: for example, the rearrangement of the diazo-compound obtained from aniline requires treatment with concentrated alkali at 130–150°C.

The converse transformation of the *anti*-diazotate to the *syn*-isomer takes place, as stated above, only in certain cases on irradiation with ultraviolet light[33]. Therefore the stereoisomeric transformation cannot be regarded as reversible. The acidification of *anti*-diazotate solutions never regenerates the *syn*-isomers, other reactions taking place.

When a proton adds to the *anti*-diazotate, an acid is formed, which, as stated above, in those cases where it could be isolated proved to have the structure of a nitrosamine:



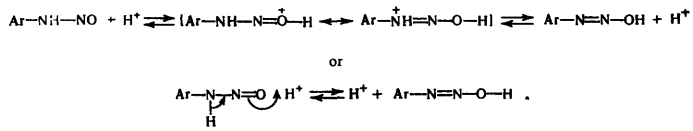
$$+ H^+ \rightleftarrows Ar{-}NH{-}NO.$$

The interaction of the nitrosamine with an acid medium leads to a gradual formation of the diazonium cation.

We may recall that an obligatory stage involving the formation of a nitrosamine with its subsequent conversion into the diazonium cation is also postulated for diazotisation, which is carried out in an acid medium. The mechanism of the transformation in an acid medium of the nitrosamine (which had acid properties) into the diazonium cation has not as yet been investigated, but kinetic methods will probably assist in its determination. However, one can now postulate that it consists in a tautomeric rearrangement of the nitrosamine into diazohydroxide, which instantaneously ionises to form the diazonium cation. We may recall that Hantzsch adhered to exactly the opposite view. He suggested that the acidification of the *anti*-diazotate yields the *anti*-diazohydroxide, which is in equilibrium with the nitrosamine. The latter rearranges via an unknown mechanism to the diazonium salt. On the other hand, one cannot postulate the preliminary formation of the *anti*-diazohydroxide in diazotisation, since the formation of the nitrosamine constitutes the first diazotisation stage.

Conversely the transformation of the nitrosamine into the diazonium cation cannot be logically imagined without the diazonium hydroxide stage, of whatever steric configuration, since on formation it should instantaneously (particularly in an acid medium) decompose into the diazonium cation.

The transformation of the nitrosamine into diazohydroxide takes place under the influence of protons. The tautomeric rearrangement presupposes the formation of an ion common to both tautomers. Thus, as stated previously, one must either postulate that the nitrosamine has minimal basic properties or that its transformation into diazohydroxide takes place by a push-pull (synchronous) mechanism. Then attack by the proton is directed to the most nucleophilic oxygen atom. The mechanism of the transformation of the nitrosamine into diazohydroxide can be represented as follows under these conditions:



$$Ar{-}NH{-}NO + H^+ \rightleftarrows [Ar{-}NH{-}N{=}\overset{+}{O}{-}H \leftrightarrow Ar{-}\overset{+}{N}H{=}N{-}O{-}H] \rightleftarrows Ar{-}N{=}N{-}OH + H^+$$

or

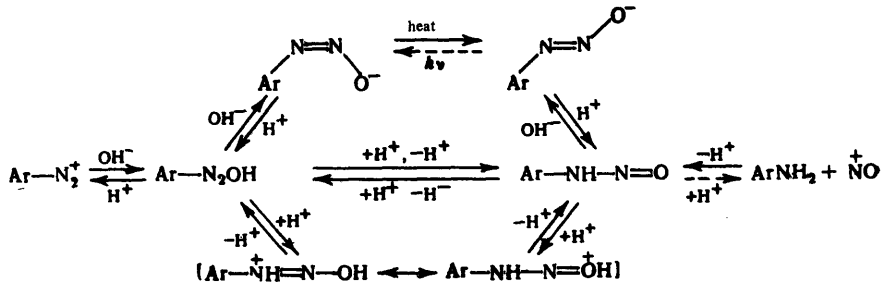
$$Ar{-}N(H){-}N{=}O \; H^+ \rightleftarrows H^+ + Ar{-}N{=}N{-}O{-}H.$$

Regardless of its steric structure, the diazohydroxide form is instantaneously converted into the diazonium cation:

$$Ar{-}N{=}N{-}OH + H^+ \rightarrow H_2O + Ar{-}N_2^+.$$

Summarising all the above considerations, one may postulate the following "cycle of transformations" of the diazo-compounds in the equilibrium systems formed in aqueous solutions of diazonium salts and by the action of alkalis on diazonium salts followed by treatment with acids.

The suggested mechanism involves protolytic, tautomeric, and stereochemical transformations, i.e. transformations of the type investigated and discussed in modern theoretical organic chemistry. It is not therefore surprising that the data collected in the study of aromatic diazo-compounds are frequently extended to other classes of organic compounds and the conclusions drawn from them are of great importance for theoretical organic chemistry.



In conclusion the author would like to deal with a minor terminological problem. Above, diazo-compounds, including in this term diazonium salts, diazohydroxides, diazotates, and nitrosamines, were considered. At the same time all these compounds differ markedly from one another in their structure: diazonium salts are indeed "diazo-compounds" since in them two nitrogen atoms replace a hydrogen atom of the aromatic ring; nitrosamines and diazohydroxide contain, in addition to the two nitrogen atoms replacing hydrogen, also an oxygen and a hydrogen atom. Diazotates contain an additional oxygen atom. Many investigators include among diazo-compounds substances in which there is a covalent bond between the terminal nitrogen atom and occasionally a very complex residue (for example diazonium sulphonates, diazonium cyanides, etc.) but do not include among them diazo-amino-compounds or azo-dyes.

To eliminate these logical contradictions, the present author believes it correct to name as diazo-compounds only substances which in aqueous or other media are involved in simple or complex equilibria with diazonium cations.

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