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THE STRUCTURE OF AROMATIC DIAZO-COMPOUNDS

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IN connexion with the structure[1] of aromatic diazocompounds it is generally accepted that:

1. The diazocompounds in aqueous solution exist as molecules and ions with their equilibrium shifted towards ionization.[2]

2. The diazohydrate is amphoteric[3] and in aqueous solutions is present in negligible amounts.

3. The diazocation and the anion have conjugated bonds.[4]

4. Only the diazocation can take part in coupling reactions.[5] This principle established independently by many authors practically refutes Hantzsch's stereoisomeric theory.

5. The diazohydrate and the nitrosaminic acid (the nitrosamine) are the tautomeric forms,[6] and in diazocompounds there are two acids (the diazohydrate and the nitrosaminic acid) and one base (the diazohydrate). This does not mean the diazocation and -anion which represent the acid and the base according to the Lewis–Ussanovitch theory.[7]

6. The reaction between the diazonium salt and alkali belongs to the class of slow ionic reactions.[8] This, together with the amphoteric nature of the diazohydrate is responsible for the most characteristic properties of diazocompounds.

Schwarzenbach[10] investigating the behaviour of dibasic aprotonic acids, showed that in some cases the second ionization constant is greater than the first. Zollinger[9] applied these considerations to diazocompounds regarding the diazocation as dibasic aprotonic acid possessing similar properties. Accordingly, in the neutralization of the diazonium salt by alkali he assumed that first stage addition of one

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[1] See the review in *Usp. Khimi.* **XXVIII**, No. 9, 1036 (1959).

[2] H. Zollinger, *Chemie der Azofarbstoffe* p. 52. Birhäuser, Basel (1958); C. Wittwer and H. Zollinger, *Helv. Chim. Acta* **37**, 1954 (1954); cf. B. A. Porai-Koshits and J. E. Bruske, *Trudy Leningrad, Tekhnol. Inst. im. Lensoveta* **60**, 92, 111 (1960).

[3] B. A. Porai-Koshits and I. V. Grachev, *Zh. Obshch. Khim.* **16**, 4 5, 571 (1946).

[4] B. A. Porai-Koshits and I. V. Grachev, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* No. 1, 137 (1938); H. Zollinger, *Chemie der Azofarbstoffe* p. 49. Birkhäuser, Basel (1958); cf. K. Holzach *Die Aromatischen Diazoverbindungen*. Stuttgart (1947); E. Müller, *Neuere Anschaungen der Organischen Chemie* 2 Aufl., p. 461. Springer, Berlin (1957).

[5] W. Dilthey and C. Blankenburg, *J. Prakt. Chem.* (2), **142**, 177 (1935); R. Wistar and P. D. Bartlett, *J. Amer. Chem. Soc.* **63**, 413 (1941); R. Hauser and D. S. Breslow, *Ibid.* **63**, 418 (1941); B. A. Porai-Koshits, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk* No. 1, 79 (1944); B. A. Porai-Koshits and I. V. Grachev, *Zh. Obshch. Khim.* **16**, 4–5, 571 (1946); C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 297. London (1953).

[6] A. Hantzsch, M. Schümann and A. Engler, *Ber. Dtsch. Chem. Ges.* **32**, 1703 (1899); A. Engler, *Ibid.* **33**, 2188 (1900).

[7] G. N. Lewis, *J. Franklin Inst.* **226**, 292 (1938); M. I. Ussanovitch, *Zh. Obshch. Khim.* **9**, 182 (1939).

[8] B. A. Porai-Koshits and B. V. Passet, *Trudy Leningrad, Tekhnol. Inst. im. Lensoveta* **46**, 133 (1958).

[9] H. Zollinger, *Chemie der Azofarbstoffe* p. 53. Birhäuser, Basel (1958).

[10] G. Schwarzenbach, *Helv. Chim. Acta* **26**, 420 (1943).

hydroxyl ion to the diazocation to form the diazohydrate would proceed more slowly that the second stage, the acidic dissociation of the diazohydrate. In this manner he proved theoretically the impossibility of isolating the diazohydrate.

It is believed that the low concentration of the diazohydrate in aqueous solutions does not depend on the properties of the aprotonic acid but results from the amphoteric nature of the diazohydrate. A detailed study of the acid–base equilibrium of the diazocation, the diazohydrate and the diazoanion, the equilibrium being complicated by the tautomeric equilibrium between the diazohydrate and the nitrosaminic acid, reveals that under certain conditions there is complete dissociation of the diazohydrate into ions.[11] These conditions are: (1) the greater magnitude of the product of the acidic and basic constants of the diazohydrate over the magnitude of the ionic product for water.

$$K_a{}'K_5 \gg K_w$$

and, (2) establishing the inequality

$$\frac{K_w{}^{2'}}{K_w} \gg \frac{K_a}{K_b}$$

where $K_a{}'$ is the ionization constant of the nitrosaminic acid.

We were able to deduce the formulae for the acidic and basic constants of the diazohydrate.

These formulae are accurate provided the dissociation constant is of the nitrosaminic acid is greater than that for the diazohydrate.

$$K_a = \frac{C\,.\,K\,.\,[\mathrm{H}^+]1}{[\mathrm{H}^+]^3{}_1 - 2C\,.\,K} \quad \text{and} \quad K_b = \frac{C\,.\,K_w[\mathrm{H}^+]1}{[\mathrm{H}^+]^3{}_1 - 2C\,.\,K}$$

C is the concentration of the diazonium salt. $[\mathrm{H}^\cdot]_1$ is the concentration of the hydrogen ions in the diazonium salt solution, K_w is the water ionic product for water and $K = [\mathrm{H}^\cdot]^2$.

In the latter expressions $[\mathrm{H}^\cdot]$ is the concentration of the hydrogen ions in the solution obtained by the addition of one equivalent of alkali to the diazonium salt, i.e., the diazonium–diazotate in solution.

It is now possible to substitute the ideas based on the theory of electrolytic dissociation for Schwarzenbach's conception as regards "the unusual properties of aprotic acid".

So far, there is no general agreement as to the stereoisomerism of the aromatic diazocompounds. As far as the stereoisomerism of covalent diazocompounds is concerned, this isomerism does not appear to be proved. Nevertheless, the resemblance of the above compounds to azo compounds whose stereoisomerism is beyond doubt[12] is probable.[13]

Although the isolation of two stereoisomeric forms of covalent diazocompounds proves the presence of stereoisomerism of the compounds involved, but it does not confirm the authenticity of the well known Hantzsch theory. This theory does not

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[11] J. E. Brüske and B. A. Porai-Koshits, *Trudy Leningrad, Tekhnol. Inst. Im. Lensoveta* **60**, 103 (1960).

[12] G. S. Hartley, *Nature, Lond.* **140**, 281 (1938); *J. Chem. Soc.* 633 (1938).

[13] R. J. W. Le Fèvre and J. B. Sousa, *J. Chem. Soc.* 3154 (1955); A. Hantzsch, *Ber. Dtsch. Chem. Ges.* **27**, 1894, 3527 (1894); A. Claus, *J. Prakt. Chem.* (2), **50**, 239 (1894).

involve the existence of stereoisomerism in general, but the correlation of the steric structure of diazocompounds and their reactivity.

It has been fully established that the only particle capable of taking part in the diazocoupling reaction is the diazonium cation. The chief argument in favour of the Hantsch theory is the supposed isolation of two stereoisometic salts.[14] Therefore, the supporters of the stereoisomeric hypothesis, linked up the alkaline "syn-salt" with the diazocation. Recently, Zollinger advanced the opinion that in aqueous solutions the equilibrium between the "syn-salt" and the diazocation is established instantly whereas that between the "anti-salt" and the same diazocation takes place slowly and from this the "apparent high reactivity of the syn-salt" results.[15]

Consideration of this statement reveals that it is based on misunderstanding: If the "syn-diazotate" changes into the diazonium cation more readily than the "anti-diazotate", the former possesses not an "apparent" but a really high reactivity.

This hypothesis supports the Hantzsch theory, as it indicates that under all conditions the solution contains the "syn-salt" rather than the diazocation.

The hypothesis of stereoisomerism of diazo alkaline salts not only explains the properties of diazocompounds but accounts for the existence of two different diazo alkaline salts.

So far the isolation of two diazo alkaline salts as two separate substances with the same composition but different properties has not been verified. Similar substances have been synthesized[16] but without any critical approach to the phenomena observed. Some workers consider that structural isomerism[17] may account for the existence of two salts. It was decided to investigate the Hantsch theory concerning the structure of the two alkaline salts and draw attention to the connection between "syn-salts" and the diazonium cation.

In order to determine if the structural isomerism of salts occurs aqueous solutions of *p*-nitrophenyldiazonium salts were titrated potentiometrically by means of the glass electrode with (1) potassium hydroxide and (2) tetra-alkyl-ammonium hydroxide (the triethyl-benzyl-ammonium hydroxide). Both titration curves were identical.[18] As the salts formed from the diazocompound and the tetrasubstituted ammonium base is completely dissociated, this must also be the case for the alkaline salt. Thus the covalent structure of the diazo alkaline salts is impossible. Hence the structural isomerism is impossible since the two acids (the diazohydrate and the nitrosaminic), being tautomeric, can yield but one salt. In spite of these considerations some investigators assume the possibility of the diazotate anions, stereoisomerism arbitrarily fixing the double bond between the nitrogen atoms in the diazotate anion.[19]

The potassium infra-red spectra of some diazocompounds show absorptions at frequencies characteristic of N-nitrosogroup (1385 cm^{-1}) but less pronounced, as well as a very slight absorption at (1574 cm^{-1}) characteristic of the azo group. At the same time N-nitrosomethylaniline and methylazobenzene, studied as standard

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[14] A. Hantzsch and D. Gerilowski, *Ber. Dtsch. Chem. Ges.* **28**, 2002 (1895); D. Gerilowski, *Ibid.* **29**, 1075 (1896); A. Hantzsch, *Ibid.* **29**, 743 (1896).

[15] H. Zollinger, *Chemie der Azofarstoffe* p. 61. Birhäuser, Basel (1957).

[16] E. Bamberger and O. Bandisch, *Ber. Dtsch. Chem. Ges.* **45**, 2055 (1912); K. H. Saunders, *The Aromatic Diazocompounds* (2nd Ed.), Chap. XI. London (1949).

[17] A. Hantzsch and G. Reddelien, *Die Diazoverbindungen*. Berlin (1921).

[18] B. A. Porai-Koshits and B. V. Passet, *Trudy Leningrad. Tekhnol Inst. im. Lensoveta* **46**, 134 (1958); *Zh. Obshch. Khim.* **29**, 1407 (1959).

[19] H. Zollinger, *Chemie der Azofarbstoffe* p. 61 *et seq.* Birkhäuser, Basel (1958).

compounds, produced quite distinct absorption bands at the frequencies indicated. This proves that there is a system of conjugated bonds in the diazotate anion resembling rather the nitrosamine than the azo compound structure. Hence, the hypothesis of the stereoisomerism of the diazotate ions should be rejected.

Titrating potentiometrically the *p*-nitrophenyldiazonium salt at different rates, curves obtained by rapid titration characterize the equilibrium not yet established. Only by special procedure were curves representing the stable equilibrium obtained.

Unfortunately, the equilibrium curve for the diazosulphanilic acid was not obtained, as in this case, the reaction between the diazonium salt and the alkali proceeds more slowly than in the case of the diazo-*p*-nitroaniline, and the diazocompound decomposes before the equilibrium has been reached.

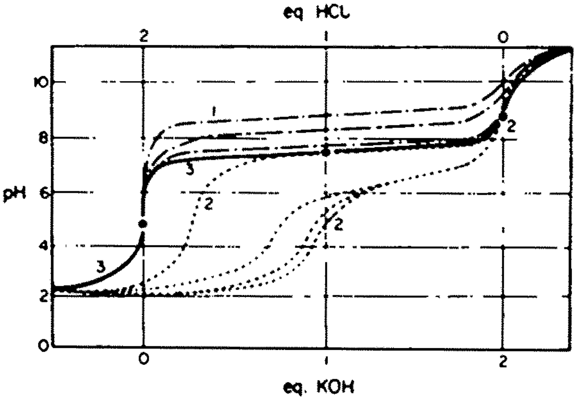

FIG. 1. The alkali and acid titration of *p*-nitrodiazobenzene at 10° at different rates.
1 the curves obtained by direct titration with alkali; the titration rates (from top to bottom); the maximum one practically got: 0·1 equiv/min; 0·04 equiv/min;
2 the curves of back titration with acid; the titration rates (from bottom to top) the maximum one practically obtained; 0·6 eq/min; 0·2 eq/min; 0·005 eq/min;
3 equilibrium curve.

The study of the electronic spectra of aqueous solutions of diazocompounds from *p*-nitroaniline, sulphanilic acid, chloranilines, aniline and many other amines in acidic and alkaline media of various concentrations show that there are isobastic points for the group of curves representing each diazocompound (see Figs. 2, 3 and 4). These isobastic points prove that in aqueous solutions there are only two substances or particles which are in mobile equilibrium. These particles in acidic and alkaline media appear to be the diazo-cation and the -anion respectively.

The isobastic points for the diazo-*p*-nitroaniline were observed independently by Lewis and Suhr[20]. They measured the absorption spectra of solutions, without providing for the equilibrium which is established and, therefore, they could neither obtain accurate results nor provide an explanation.

In accordance with the results of spectral analysis we developed a method of separate quantitative estimation of diazocation and concentrations in solution for diazo-*p*-nitroaniline[21] and diazosulphanilic acid.[22]

As all this work has been carried out with aqueous (in some cases alkaline) diazosulphanilic acid solutions (e.g. while studying electronic spectra) and other

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[20] E. S. Lewis and H. Suhr, *J. Amer. Chem. Soc.* **80**, 1367 (1958).
[21] B. A. Porai-Koshits and B. V. Passet, *Zh. Prikl. Khim. iss.* **11**, 2580 (1959).
[22] B. A. Porai-Koshits and Ching Kvrn Tay, *Trudy Leningrad, Tekhnol. Inst. im. Lensoveta* **60** (1960).

compounds but not with the "syn-salt" synthesized by Hantzsch, we considered the investigation of Hantzsch "syn-salt" very important.

Accordingly, the "syn-salt" indentical in all respects with that described by Hantzsch[23] was prepared. Its most important property, viz, the capacity of entering into the diazocoupling reactions, depends both on the method of preparation and on the length of time of keeping. Thus, having been isolated and rapidly filtered, the preparation possesses the capacity of diazocoupling, the yield of azo dyes being nearly quantitative. Dried to constant weight and prepared for elementary analysis (according to Hantzsch) the "syn-salt" exhibits only 11–15 per cent diazocoupling. After keeping for half a year it completely loses the capacity of diazocoupling.

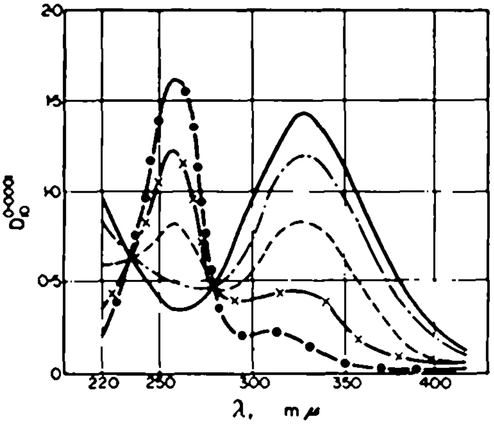

FIG. 2. The *p*-nitrodiazobenzene aqueous solutions absorption curves at various values of pH.
—·—·—·— pH = 4·0; --×—×--×—· ph = 7·38; — — — — pH = 7·67;
—●— ● —●— pH = 7·98; ———— pH = 11·0

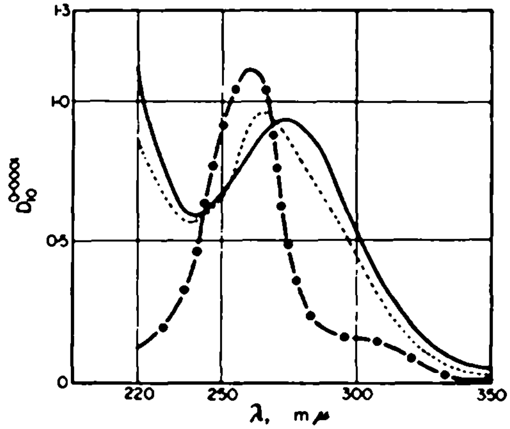

FIG. 3. The diazobenzene aqueous solutions absorption curves at various values of pH.
-●—●—● pH = 3·0; .... pH = 9·0; — — - - pH = 11·0

Hence, according to the period of keeping there are various forms of the "syn-salt" differing from one another in their capacity to enter into the diazocoupling reaction.

[23] A. Hantzsch and D. Gerilowski, *Ber. Dtsch. Chem. Ges.* 28, 2002 (1895).

Since only the diazocation takes part in the diazocoupling reaction it was concluded that the "syn-salt" prepared for analysis consisted of 11–15% diazonium salt with the required amount of the alkali and the diazo alkaline salt. Comparing the results of our own elementary analyses with those of Hantzsch this conclusion was confirmed.

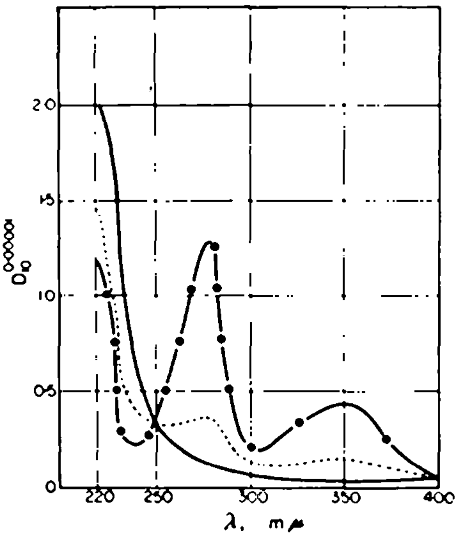

FIG. 4. The 2,6-dichlordiazobenzene aqueous solution absorption curves at various values of —●—●—●— pH = 4·0; .... pH = 7·7; - ——— pH = 11·0

Hantzsch considered the "syn-salt" as homogeneous and in order to accept the analytical data obtained, he supposed that the "syn-salt" crystallized with 1·5 molecules of water.

By means of diazocoupling in buffer solutions with 2-naphtol and the subsequent colorimetry of the solutions obtained, our assumption that the analytical sample of "syn-salt" was a mixture of substances has been confirmed. The sample contained 11·3 per cent of the diazonium salt.

In addition, a sample of this "syn-salt" was titrated with phenyl-methyl-pyrozolone-sulphonic acid following the usual procedure adopted for the determination of diazonium salt,[24] and the results obtained show 11·4 per cent of diazonium salt.

Another sample of the "syn-salt" containing 31 per cent of the diazonium salt (According to phenyl-methyl-pyrozolone-sulphonic acid titration), was titrated potentiometrically and polargraphically and the percentage diazonium salt confirmed. The so-called "anti-salt" (i.e. an ordinary diazo "alkaline salt") showed no oxidizing properties during the titration and the diazocation produced a curve the height of which corresponds to the quantity of the diazocation in the solution. These results are in accordance with Hodgson and Marsden[25] who showed that the "syn-salt" is reduced by sodium-stannite while the "anti-isomer" fails to enter into this reaction.

In order to reject the conception of "instantly set in equilibrium syn-salt-diazocation" we obtained the electronic absorption spectra of the diazonium salt from the

[24] I. V. Grachev, *Factory Lab.* **2**, 154 (1945); *Ibid.* **4–5**, 435 (1946).
[25] H. Hodgson and E. Marsden, *J. Chem. Soc.* 207 (1945).

sulphanilic acid (i.e. in acidic media), the "anti-salt" (in alkaline media), the "syn-salt" (containing 11·3 per cent of diazonium salt) and the diazonium salt mixtures with the "anti-salt" at pH corresponding to the "syn-salt" solution. The "syn-salt" absorption curve coincided with the mixture curve of the diazonium salt and "anti-salt" containing 11·5 per cent of diazonium salt (Fig. 5) and hence, Zollinger's considerations are invalid.

Instead of the "stereoisomeric" hypothesis which has not been confirmed we suggest that the properties of aromatic diazocompounds depend on a state of complex equilibria as follows:*

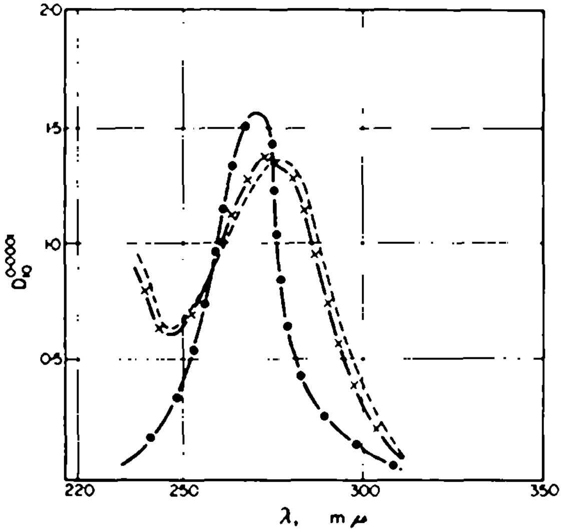

Fig. 5. The p-diazobenezenesulphonic acid aqueous solutions absorption curves. —●—● ●– The cation absorption curve (acid medium) · --- · the so-called "syn-salt" absorption curve at pH · 10·0. · ×—×—×– · the points of the curve representing the 11·5% diazonium salt with 88·5% "anti-salt" and alkali mixture. · · ·--- · the anion absorption curve (alkali medium).

$$R{-}N\ \ N{-}Ac \underset{Ac^-}{\overset{H^+}{\rightleftarrows}} R{-}N_2^+ \underset{H^+}{\overset{OH^-}{\rightleftarrows}} R{-}N\ \ N{-}OH \underset{H^+}{\overset{OH^-}{\rightleftarrows}} R{-}N_2O \underset{OH^-}{\overset{H^+}{\rightleftarrows}} R{-}NH{-}NO$$

The position of the first partial equilibrium in this general equation

$$R{-}N{:}\ \ N{-}Ac \rightleftarrows R{-}N_2^+ \cdot\cdot\ Ac^-$$

depends on the strength of the acid HX.[26] The weaker the acid the more this equilibrium is shifted to the left and the equilibrium constant for acetic acid according to De-Tar[27] is less than $10.^5$

Hence by applying weak acids, such undissociated substances as diazoacetate, diazocyanide and diazosulphonate etc can be isolated. Evidently stereoisomers are likely to be found among these covalently built substances.

The application of strong acids shifts this equilibrium to the right; the decrease

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* These equilibria have been previously discussed.

[26] A. Hantzsch, *Ber. Dtsch. Chem. Ges.* 33, 2179 (1900); A. Hantzsch and H. Euler, *Ibid.* 34, 4166 (1901).

[27] D. F. De-Tar, *J. Amer. Chem. Soc.* 77, 1745 (1955).

and solubility of the diazonium ionized salts favours the isolation of co-called "active" stable diazocompounds. This has application in industry and the compounds may be isolated as sulphates,[28] salts of aromatic sulphonic acids [29] or in the form of double salts with the salts of tin,[30] zinc[31] or other metals.[32]

On account of the amphoteric nature of the diazohydrate the following partial equilibrium between the diazonium cation and the diazohydrate is inseparable from the equilibrium between the diazohydrate and the diazotate anion and is perhaps the most important conversion of diazocompounds:

$$R{-}N_2^+ \xrightleftharpoons[H^+]{OH^-} R{-}N{=}N{-}OH \xrightleftharpoons[H^+]{OH} R{-}N_2O$$

In this equilibrium, the reaction between the diazocation and the hydroxyl ion, proceeds more slowly than the subsequent interaction between the diazohydrate and the second hydroxyl ion. Consequently the equilibrium is established slowly and eventually the solutions do not contain any diazohydrate. For some diazocompounds the above equilibrium was studied quantitatively, the spectral method being applied for determining the quantities of the diazonium cation and the diazotate anion. In the case of diazo-*p*-nitraniline this equilibrium constant[21] was found to be K $6{\cdot}3.10^{16}$.

The slowness of the first stage of the equilibrium is responsible for "the existence of two alkaline salts" and the "syn-salt" is therefore a mixture. The diazonium salt and the alkali react even in the solid state producing the alkaline diazocompound salt. All the properties of the "syn-salt" are in agreement with this approach.

The last partial equilibrium:

$$R{-}N_2O^- \xrightleftharpoons[OH^-]{H^+} R{-}NH{-}NO$$

represents the dissociation-molarization of the nitrosaminic acid. It is characteristic of the tautomeric equilibrium between the nitrosaminic acid and the diazohydrate. Increased alkalinity of the medium shifting the equilibrium towards the diazotate anion which may be isolated by decreasing the solubility of the diazocompound alkaline salts. Such preparations[33] are known as "nitrosamines" and "antidiazotates", names we consider as incorrect.

The alkaline salts of the diazocompounds have found application in the dyeing industry as "passive" stable diazocompounds,[33] i.e. substances which cannot undergo the diazocoupling reaction because they do not contain any diazocation. After treatment with acids these alkaline salts are changed into the diazocation and acquire activity.

In some cases by rapid acidification of the diazocompound alkaline solutions, it is possible to isolate the unstable nitrosaminic acids ("free nitrosamines"). Gradually the nitrosaminic acid precipate dissolves, a spontaneous increased pH of the

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[28] Brit. Pat. 21227/94 (M L B); Ger. Pat. 85387 (M L B); *Frdl.* **4**, 673s (1899) Ger. Pat. 622306 (I.-G); *Chem. Abstr.* **30**, 5803¹ (1936).

[29] Ger. Pat. 81039; *Frdl.* **4**, 673 (1899).

[30] P. Griess, *Ber. Dtsch. Chem. Ges.* **18**, 965 (1885).

[31] Ger. Pat. 484894 (I-G); *Frdl.* **15**, 569 (1928).

[32] A. N. Nesmejanov, *Ber. Dtsch. Chem. Ges.* **62**, 1018 (1929); *Ibid.* **68**, 1877m (1935).

[33] C. Schraube and C. Schmidt, *Ber. Dtsch. Chem. Ges.* **27**, 514 (1894).

medium taking place. This confirms the idea that the equilibrium between the alkaline salts of the diazocompounds and the mineral acids as well as between the diazonium salt and the alkalis takes place slowly as established by potentiometric titrations.[21]

All the puzzling chemistry of diazocompounds is understood if we take into consideration the amphoteric nature of the diazohydrate, the tautomerism between the diazohydrate and the nitrosaminic acid and, finally, the slowness of some neutralization ionic reactions[34] in particular the reaction between the diazonium cation and the hydroxyl ion.

The only conception of former views which should be retained is the stereoisomerism of the covalently built diazocompounds (such as the diazocyanides, the diazoacetates, etc). But this is beyond the scope of the Hantsch theory and concerns phenomena frequently met in organic chemistry.

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[34] O. F. Ginsburg, *Zh. Obshch. Khim.* 23, 1504, 1677 (1953); A. A. Frost and R. G. Pearson, *Kinetics and Mechanism* p. 113. McGraw-Hill, New York (1953).