The Hantzsch Memorial Lecture.

ARTHUR RUDOLF HANTZSCH.

1857—1935.

A MEMORIAL LECTURE DELIVERED AT THE UNIVERSITY OF BRISTOL ON APRIL 16TH, 1936.

By T. S. MOORE.

ARTHUR HANTZSCH was born in Dresden on March 7th, 1857. His father was a wholesale dealer in wine, carrying on a business which had been founded by his great-grandfather, originally a cooper, and his mother was the daughter of an artist, Professor J. U. Bähr, of Riga. According to his own account, Hantzsch was an emotional child, with little self-reliance. His strongest childish interest was in animals, both extant and prehistoric, and this carried him on to the study of zoology and botany in his school and Gymnasium period, during which he developed also an aptitude and liking for languages. The sound of spoken Greek, in particular, appealed to him, and though he did not take Greek as a school subject, he preferred it much to Latin, and studied it privately. Chemistry was not taught at the Gymnasium, but Hantzsch must have had some contact with the subject from quite an early age, for he has recorded that during his Gymnasium period this subject, which in childhood had seemed mysterious, gradually replaced zoology as a main interest, and that he made attempts to carry out chemical experiments for himself. On the other hand, he neglected subjects in which he was not interested, and left the Gymnasium in 1875 with only a moderate certificate.

In the same year Hantzsch began his serious study of chemistry under Professor R. Schmidt and Dr. W. Hempel at the Polytechnikum (now the Technische Hochschule) in Dresden. Schmidt, a pupil and later an assistant of Kolbe, is described as a man of great ability, and was best known for working out a successful large-scale process for the production of salicylic acid by Kolbe's reaction, and for his discovery that phenol sodium carbonate is an intermediate product in the synthesis. He was one of those who, led by Hofmann, founded the German Chemical Society. Hantzsch received the greater part of his formal scientific training under Schmidt and his colleagues, for although he took his doctor's degree in Würzburg in 1880, he worked there under Wislicenus during only one semester. His thesis for the doctorate was on " paraoxyphenetol and some aldehydes and ketones derived from hydroquinone "; his subsidiary subjects were physics and mineralogy, and he was classed " summa cum laude." One of his contemporaries in Würzburg remembers Hantzsch at this time as an extremely hard worker, mixing little with his fellow students and apart from his research work much preoccupied with his engagement—dating from 1879—to the eldest daughter of the sculptor Johannes Schilling, to whom she served as model for the figure " Germania " in the Niederwald monument.

The summer of 1880 Hantzsch spent in Hofmann's laboratory in Berlin, working on small researches which formed the subjects of his first two papers, and in the autumn of the same year he became an assistant under Wiedemann in the physical chemistry laboratory in Leipzig. This appointment had a great effect on his career. In Wiedemann's laboratory he was brought into intimate contact with physical problems and methods, and his reaction to this new influence is indicated by the fact that when he became " Privat-docent " in 1882 the subject of his " test " lecture was " the relation between physical properties and chemical constitution." But in research he continued as a pure organic chemist, publishing as his " Habilitationsschrift " in 1882 his remarkable work on the synthesis of compounds of the pyridine series from acetoacetic ester and aldehydes. This work, probably the most striking single advance ever made in pyridine chemistry, at once established Hantzsch among the foremost young chemists of his time, and all the more because the circumstance of his working alone as an organic chemist in a physical chemistry laboratory emphasised his independence and originality. It brought him not only his appointment as " Privat-docent " two years after he had become assistant, but also an invitation, at the remarkably early age of 28, and without his having passed through the stage of "ausserordentlicher" Professor, to a full Professorship in the Polytechnikum at Zürich in succession to Victor Meyer. Hantzsch ascribed this appointment to a lucky chance, for although four of the leading German professors consulted by the Swiss authorities each recommended as first choice a different candidate (in two cases, their own sons-in-law), as second choice all independently recommended him.

Hantzsch's eight years in Zürich were fortunate and happy. He had been married in 1883, and his two daughters and one son were born in Zürich; his work, particularly his investigation of the oximes, gave him a world-wide reputation, and attracted students from many countries. In the Swiss mountains he found both æsthetic and physical satisfaction, and the freedom of religious and political opinion in Switzerland was in accord with his own liberal outlook. Throughout his life, and not least at the end, the Swiss Federation was for him the pattern of national and social organisation. He called Switzerland his "zweite Heimat," and few of his vacations in later life were spent elsewhere.

In 1893, having already declined invitations to Chairs in Kiel, Worcester (Mass.), and Rostock, he left Zürich to succeed Emil Fischer in Würzburg, and there he spent what he afterwards referred to as the happiest and most care-free period of his life. Like Fischer before him, he found Würzburg a friendly place, with easy and stimulating intercourse among all ranks in the University, from professors to students. His first task in Würzburg, as it had also been in Zürich, was to superintend the erection of a new laboratory already planned by his predecessor, and though he made no alteration in Fischer's general plan, of which spaciousness and airiness were the novel and principal features, he took great care in the design of the fittings and increased the accommodation for physico-chemical work. Nearly thirty years after it was built Fischer recorded his opinion that the Würzburg laboratory was still one of the best in Germany.

After considerable hesitation, Hantzsch left Würzburg in 1903 to succeed Johannes Wislicenus in Leipzig, where for twenty-five years he directed a continually increasing number of students who came to him from all over the world. His wife died in 1904. He remained a widower for seven years and then married Hedwig Steiner of Zürich. The three children of his first marriage were themselves married in this period, and his son, who as a very young man served in the Great War, was killed in 1921 on the Grossglockner in an attempt to help other climbers who were in danger.

Hantzsch's 70th birthday, in 1927, was marked by a festival attended by representatives of Universities and scientific Societies, by colleagues and by a large number of his former students, and in commemoration a bronze portrait medal was struck. To Hantzsch himself and to his family, this was one of the greatest events of his life, and for his remaining years the recollection of the respect and affection manifested by his former students on this occasion was an abiding pleasure. Shortly after his 70th birthday Hantzsch was retired from his Professorship, and his second wife died in the following year. He then removed to Dresden, choosing, for the sake of its old associations, a house in the neighbourhood of the Gymnasium he had attended as a youth. No longer responsible for the direction of a large laboratory, and without the companionship of his wife, his researches became his only occupation, and he visited Leipzig frequently to supervise the work of his assistants. His mind continued as vigorous as ever, and indeed his old age brought him no worse ill than mild rheumatism and some loss of memory, which, however, was more apparent to himself than to others. In happy intercourse with his children and grandchildren and his few intimate friends, and active in his work, he passed an enviable old age, closed by his death on March 14th, 1935, at the age of 78.

Hantzsch received honorary degrees from the University of Leipzig and the Technische Hochschule of Dresden, and was nominated Geheimer Hofrat in 1908. He was Vice-President of the German Chemical Society from 1919 to 1921, and thereafter a permanent member of its Council. In 1929 he was elected an Honorary Foreign member of our Society, and on this occasion wrote letters to the Council and to some of his English students showing the highest appreciation of the honour.

A. Hantzsch

[*To face p.* 1052.

Hantzsch was a reserved and sensitive man. Only those who were admitted to his home, and saw him among his family and his few intimate friends knew him for a devoted husband and father, entirely happy in his family relations, enjoying with an attractive simplicity the occupations of the family circle. To his guests he was a vivacious and charming host. He had interests in philosophy and music and art and especially in poetry, but the one strong intellectual preoccupation in his life was chemistry. Yet he kept his work as a chemist strictly separate from his private life; his daughter writes that not once, even in the narrowest family circle, did she ever hear him refer to his work or to the fame it had brought him. In the laboratory, intercourse with him on chemical matters was easy and friendly, for he disliked formality, and in 1908 when he became " Geheimer Hofrat " asked that he might still be " Herr Professor " to his students. But although until late in life he neglected no opportunity of mixing with his students, he rarely appeared to be at ease among them on social occasions, and only in a few cases was the relation of professor and student succeeded by one more intimate. None the less he had a great personal interest in his students, and nothing gave him more pleasure in his later years than visits and letters from them.

All his life he was abstemious, a non-smoker and using wine only sparingly—a quarter of a litre, generously diluted with water, sufficing for a whole evening. In his younger days he kept himself fit by gymnastics, cycling, and climbing in Switzerland in the vacations, and throughout his life enjoyed very good health. Tall and spare in figure, moving with long springy steps, rapid in speech and action, and showing his feelings as much by his expression as his words, he gave an unforgettable impression of vigour and nervous energy.

His lectures on general organic chemistry, enlivened by his enthusiasm and by touches of simple, rather sly, humour, were original and stimulating. Usually he made a round of his research students twice a day. When a negative was returned to his customary " have you found anything new? " he passed on, unless the student wanted help, but if there was something new, he would stay, examining specimens and discussing results, very willing to hear the student's views and free in expressing his own. Frequently he would bring out one of the little note-books he always carried, and provide some new references or some wholly fresh idea. A visit from Hantzsch was usually encouraging, but occasionally his obvious disappointment at delay in getting results or at results which did not fulfil his expectations was disconcerting, and in a few cases, where researches which had gone too far to be abandoned proved to be of no value in relation to his purpose in the investigations, his interest in them died away and his visits to the students concerned lost greatly in value. Hantzsch seldom after his earlier years did any experimental work himself, and only in special cases gave precise direction for experimental methods. He assumed that students admitted to do research were capable of maintaining a high standard, and that their recorded results had been reached by accurate methods impartially applied, so fostering in them independence and self-reliance.

Few, if any, chemists have surpassed Hantzsch in the number and vigour of their controversies. To appreciate the reason for this it is necessary to realise that Hantzsch's approach to a scientific problem was as much a novelty as the experimental methods he employed in its investigation. It was precisely in this method of approach that Hantzsch's special genius lay. He employed induction on the grand scale, arriving apparently intuitively at generalisations which must in reality have been based on the correlation of numerous small and disconnected observations—a method quite unlike the step-by-step deductions of synthetic organic chemistry as it was then practised or the inductions from large bodies of well ascertained facts such as those associated with the names of Kekulé, van 't Hoff, and Arrhenius. A distinguished former student compares his method to the operation " of the feminine instinct, which is often right though without logical support "; a former colleague and an intimate friend thought Hantzsch a poet rather than a mathematician. So it came about that in the first exposition of his new theories he frequently quoted in their support a number of weak arguments valuable only because they all tended in the same direction, and he always extended his generalisations over the widest possible field. His arguments were often individually vulnerable and his first generalisations too wide, provoking criticism from other chemists whose smaller fields they happened to touch. His style of writing, assured and sometimes didactic, was in itself provocative. Thus while Hantzsch with his collaborators went on to investigate in great detail the whole range of chemistry to which his generalisations might apply, he was under the necessity of replying to criticisms which, though justifiable, and valuable in that they exposed weaknesses, were often misconceived in that they purported to condemn the whole structure which he had raised, whereas in fact they removed only a few weak props. As a result of his own investigations, and to a smaller extent on account of the work of other chemists, his views in many cases became modified, though still retaining the central original ideas. It can be said that no chemist with a reputation to lose committed so many errors as Hantszch. But the method to which these errors were incidental led also to advances in the science so fundamental that our present outlook on almost any problem of organic chemistry, whether Hantzsch worked on it or not, is largely dependent upon them.

Hantzsch's eager temperament made him severe and persistent in controversy, but those who knew him cannot doubt that whether in criticising or in rebutting criticism, his strongest motive was his desire for scientific truth. An examination of the literature shows that, when personalities occurred in his controversies, they were introduced by his opponents. There can be no doubt either that he disliked and even resented criticism, but his irritation seldom survived the controversy, and in almost all cases friendly relations were resumed even with his most bitter critics.

Synthetical Work.

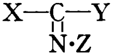
Hantzsch's researches up till 1890 may be classed as synthetical, though synthesis was not their primary object. He thought that if the " chemical mimicry " discovered by V. Meyer to exist between thiophen and benzene should occur over a range of substances, it would throw much light on relations between properties and constitution, particularly in the aromatic series. By new synthetical methods he prepared thiazole and its homologues, which were extraordinarily similar in properties to the corresponding pyridine derivatives, and later the analogous compounds in which the sulphur is replaced by selenium, oxygen, or the imino-radical—the selenazoles, the oxazoles, and the iminazoles. Original and expert in synthesis as Hantzsch proved himself to be by this work, he was not strongly interested in structure as such, but in developing the ideas on structure so that all the properties of a compound and not merely its chemical relationships could be expressed in its constitution. With the commencement of his work on oximes in 1890 his synthetical work was broken off and never resumed.

Oximes.

Before the publication of the Hantzsch–Werner paper on oximes the exhaustive investigations of V. Meyer had made it clear that the classical theory of structure would not account for the existence of three dioximes and two monoximes of benzil, and V. Meyer and Auwers had put forward the view that restricted relative rotation of the two singly linked carbon atoms might be the cause of the existence of structurally identical isomerides in this case. The discovery of a second benzaldoxime did not at once make this view untenable, for alkylation experiments appeared to show that the second benzaldoxime is a structural isomeride of the first, and Goldschmidt's proof that both react as hydroxyl compounds with phenyl *iso*cyanate was not immediately accepted.

Perhaps the most remarkable feature of the Hantzsch–Werner paper is that a theory of such importance was put forward with so little experimental support. The strongest argument advanced by the authors in favour of their hypothesis that the three valencies of tervalent nitrogen are not necessarily in the same plane, was that it gives an explanation of the isomerism of the oximes without involving a departure from the theory of structure which had interpreted satisfactorily all earlier cases of isomerism. But in contrast with the enormous number of cases of isomerism in compounds containing the groups $>C=N-$, $-N=N-$, Nabc and abN—Ncd, which, as the authors pointed out, might be expected on their theory, they were able to quote as actual examples only the isomeric oximes of benzil, the isomeric benzaldoximes (since they accepted Goldschmidt's proof of structural identity), and two oximinosuccinic acids, for the structural identity of which there was some evidence. Certain hydroxamic acids, and *p*-azoxybenzene, which had been mistakenly reported as existing in isomeric forms, were also mentioned as being possibly examples of similar isomerism. Hantzsch and Werner were aware, of course, that far more evidence was necessary to establish their theory, and explicitly put it forward as an idea worthy of further investigation rather than as a view to be accepted immediately.

A note appended to this paper, describing Werner's part in it and signed by Hantzsch alone, throws some light on Hantzsch's character. It runs as follows :—" Finally, in the event of the above argument becoming recognised as having significance, the undersigned is only fulfilling a duty in stating that this theory, published in common with Werner, is in all essential his. He had already formulated the central idea with its most important consequences when I first expressed the vague idea that nitrogen, just as well as carbon, might give rise to geometrical isomerism."

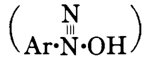
Great as was Werner's share in the formulation of the new theory, the experimental proof was due wholly to Hantzsch's energy and experimental power. In one year, working with substances frequently extremely labile and undergoing transformation under unprecedented conditions, he with his collaborators accumulated overwhelming evidence both for the tautomerism and for the stereoisomerism of the oximes. Adopting methods similar in principle to those used by Wislicenus in his work on the geometrical isomerism of unsaturated carbon compounds, he had further arrived at configurations for the aldoximes, and by the use of the Beckmann reaction under controlled conditions had not only obtained a new line of evidence for the structural identity of isomeric ketoximes, but had deduced configurations for them, apparently with certainty. On the other hand the concurrent search for isomerides of the types  $X-\underset{\overset{\|}{N\cdot Z}}{C}-Y$ (where Z is a group other than OH, OAlk, or OAr) and Nabc proved at that time fruitless.

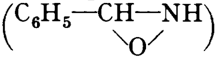
The restriction of the proved cases of isomerism to oximes and their immediate derivatives was a sufficient reason to V. Meyer and Auwers for not accepting the Hantzsch–Werner hypothesis, and even the discovery of isomeric hydrazones, which soon followed, did not convince them. A controversy arose which is now only of interest for the courtesy displayed on both sides. Each expressed their admiration for the work of the other, and though unconvinced of the truth of the opposing view, admitted its possibility.

Since 1894, it has been necessary to make only one important modification in the chemistry of the oximes. Hantzsch's deductions on configuration depended on the truth of the principle first enunciated by Wislicenus that " intramolecular reactions are the more likely to occur, the nearer the reacting groups." Except in the case of the benzildioximes, where the configurations as determined by the Beckmann reaction did not agree with those deduced from relative ease of anhydride formation, the results Hantzsch obtained by the application of different methods were consistent, and they were universally accepted for nearly 30 years, in spite of the recognition by Werner and a few other chemists that the Beckmann change might involve a " *trans* "-reaction. That this is actually the case, and that nitrile formation from aldoximes is also a " *trans* "-reaction followed conclusively from the work of Meisenheimer in 1921. Thus Hantzsch's " *syn* " series is really " *anti* " in configuration, and vice versa. It is doubtful whether Hantzsch himself ever accepted fully Meisenheimer's conclusions, for in one of his later papers (1930) where he opposed with his customary vigour a suggestion that stereochemical formulæ for oximes are unnecessary, he quoted the benzaldoxime which readily gives benzonitrile as the one in which the hydrogen and the hydroxyl group are in the *syn*-position.

Diazo-compounds.

The scientific investigation of the diazo-compounds commenced with v. Pechmann's discovery in 1892 that diazobenzene on benzoylation gives nitrosobenzanilide. In 1894 the *iso*diazotates were discovered independently by Schraube and Schmidt, v. Pechmann and Frobenius, and by Bamberger, and nitrosoamines obtained from them by alkylation.

All these authors agreed in regarding *iso*diazo-compounds as nitrosoamines (Ar·NH·NO), while the normal diazo-compounds retained the true diazo-formula (Ar·N=N·OH) assigned to them by Kekulé and confirmed by E. Fischer's proof that on reduction they give hydrazines—a reaction by which the diazonium formula of Blomstrand, Strecker, and Erlenmeyer  $\left(Ar\cdot\overset{\overset{N}{|||}}{N}\cdot OH\right)$ was supposed to be disproved. The salts from normal diazo-compounds with strong acids and strong bases were thought to belong to the same structural type (Ar·N=NCl, Ar·N=N·OK).

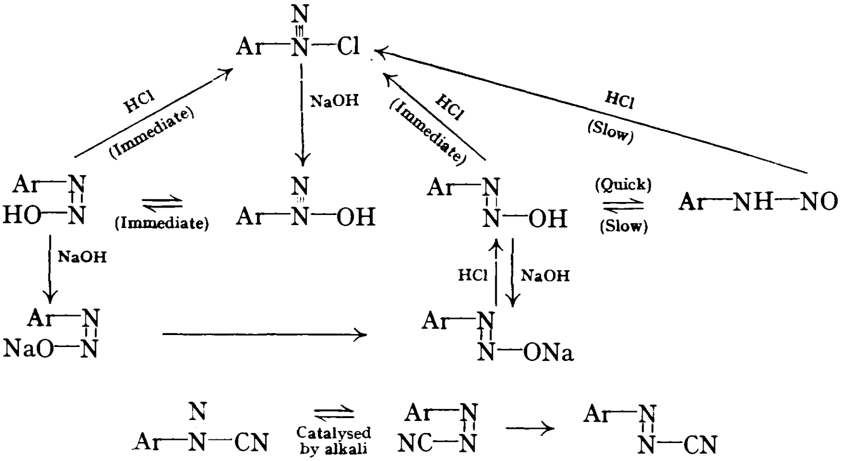
Hantzsch's first paper on the diazo-compounds (1894) resembles the first paper on oximes in that a new theory is put forward on very little experimental evidence, but differs from it in that the new theory is stated didactically, as if it were completely proved. The existence of two isomeric forms of diazoaminobenzene, and of a second potassium diazobenzenesulphonate comprised the whole of the new experimental evidence, and of this the first item soon disappeared, for Bamberger showed that the alleged isomeride was in reality a bisdiazoamino-compound. The new diazobenzenesulphonate was excessively unstable, and the only evidence of its formula was analyses which were unconvincing because they gave concordant results only if they were carried out under special conditions. On the other hand, the general arguments in the paper are very strong. The existence of geometrical isomerism in ethylenic compounds, with the group $>C=C<$, and in oximes, with the group $>C=N-$, afforded, according to Hantzsch, a strong presumption that similar isomerism will occur in compounds containing the group $-N=N-$, and that isomerism found among diazo-compounds may well be due to this cause. Further, the historical parallel between the development of the chemistry of the oximes and that of the diazo-compounds gave, in Hantzsch's opinion, strong support to the idea that the combination of stereoisomerism and tautomerism which operates in the oximes is responsible also for the behaviour of the diazo-compounds. Thus, the second benzaldoxime had been wrongly given a special formula  $\left(C_6H_5{-}\underbrace{CH{-}NH}_{O}\right)$ on the basis of alkylation experiments; in the diazo-series, the newly discovered *iso*diazobenzene, again on the basis of alkylation experiments, had been given the formula $C_6H_5{\cdot}NH{\cdot}NO$. But, just as the oximes can give *O*- or *N*-ethers according to the conditions of alkylation, so the *iso*diazo-compounds give *O*- or *N*-derivatives according to the method used. Hantzsch maintained that such alkylation experiments proved the tautomeric nature of the diazo-compounds but not their constitution, and in this connexion made the following significant remark : " It must become more generally recognised that we cannot explain chemical reactions by structural formulæ, for by them one can represent only the initial and the final state of a system. And even the possibility of this will become the smaller, the further we depart from the chemistry of carbon, in which the theory of valency founded wholly on structure has proved so valuable, and go over into the chemistry of other elements."

In arguing against the formulation of normal and *iso*diazotates as structural isomerides $C_6H_5{\cdot}N{=}N{\cdot}OK$ and $C_6H_5{\cdot}NK{\cdot}NO$ Hantzsch made two further general statements which, like that just quoted, show how far his ideas were in advance of those prevailing at the time. After pointing out that the alkali metal, which has little affinity for nitrogen but much for oxygen, would not be expected to migrate from the latter to the former in the formation of an *iso*diazo-compound, he said :—" According to my belief, not only do the alkali-metal compounds of acidic esters (acetoacetic ester, malonic ester, etc.) have the alkali metal attached to oxygen (or more correctly in the sphere of affinity of the oxygen), but also the alkali-metal compounds of acid amides, of urethane and even of nitroethane." And again, pointing out that two such salts would constitute the first example of structurally isomeric salts, and citing Werner's work on the metal-ammines, he states " Isomerism is never found, and therefore seems not to exist, where the cause of isomerism would be a difference in the mode of attachment of an atom or group capable of splitting off as an ion "—a generalisation which, to judge by formulæ even now appearing in the literature, has not yet received complete recognition.

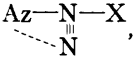
Such arguments had little effect at the time. For most contemporary chemists all that Hantzsch had done was to show formally that the stereochemical explanation which had succeeded for the oximes might apply also to the diazo-compounds. The extreme difference in stability between the normal and the *iso*diazotates and between the two potassium diazosulphonates appeared to them to be far too great for substances of the same structure, differing only stereochemically.

The controversy with Bamberger which followed has fortunately no parallel in chemical literature. Bamberger, undoubtedly a great organic chemist, was much more concerned with arguments on particular points than with the generalisations which, for Hantzsch, formed the essential structure of chemistry, and not always understanding the physico-chemical arguments which became so important in this problem, distrusted deductions from them. He did not conceal his satisfaction that he used only " the methods of pure organic chemistry." In a sense, the controversy was not only between an experimentalist and a theorist, but between the ideas of traditional organic chemistry and the wider views of the science of which Hantzsch was the first exponent. It is due to Hantzsch's memory to record that the acrimonious tone of this dispute did not arise through him. Bamberger's first critical paper was quite as didactic in tone as Hantzsch's statement of his theory, but there is in it an undertone of irritation and antagonism which was not imitated by Hantzsch in his reply. Later, when Bamberger's terms became insulting, Hantzsch permitted himself from time to time a sharp retort, but in the main his papers are confined to scientific controversy, vigorous in its expression, but seldom impolite.

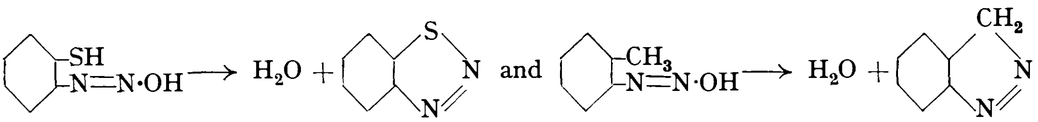
Almost the whole of the experimental work on which the accepted theory of the diazo-compounds is based is due to the work of Hantzsch and his collaborators. A great deal of our knowledge of the diazo-ethers, the diazo-hydroxides, and the nitroamines is due to Bamberger, but neither this important work nor his frequently unsuccessful repetition of Hantzsch's experiments contributed essentially to the solution of the problem. The substances Bamberger worked with were mainly explosive when isolated, usually decomposed rapidly in solution and apart from decomposition changed easily into isomeric forms which in many cases showed tautomerism. Hantzsch, on the other hand, widened the experimental basis of his research in every possible direction, seeking in each class of substances for its most stable member, and since he was convinced on general grounds that tautomerism played a great part in the reactions, allowed for this in his choice of experimental conditions and in the interpretation of his results. Gradually he built up a technique which, on the organic side alone, is a marvel of insight and ingenuity. Even more important historically is the decisive part played for the first time in this research by physical methods of investigating organic problems. Actually, only cryoscopic measurements and determinations of electrical conductivity were used at all widely, but these showed with certainty the presence or absence of electrolytic dissociation, the number of ions into which a molecule dissociates, the strength of the substances as acids or bases, and changes of electrolyte into non-electrolyte and the reverse—points which, in fact, were crucial. By 1902, after 8 years of intense activity, Hantzsch had arrived at the results expressed in the following table :



In 1912, an extensive investigation of the ultra-violet absorption spectra of azo- and diazo-compounds confirmed this scheme of structure in almost every particular. On one point there was divergence, for the only *syn*-diazotate stable enough for spectroscopic investigation did not show the band found to be characteristic of the $-N{=}N-$ group. To this extent the constitution of the most unstable class of diazo-compounds is uncertain.

Until 1912 Hantzsch had to defend his views against many critics, and even as late as 1930 alternative formulæ were advanced. A point emphasised by British critics in particular is that Hantzsch's formulæ are applicable to aromatic and aliphatic compounds equally, whereas only aromatic diazonium compounds can be isolated. On account of the absorption spectra, which excluded the quinonoid formulation proposed by some British chemists but indicated a modification of the absorption of the aromatic residue, Hantzsch wrote the diazonium formula  $\mathrm{Az{-}\overset{}{N}{-}X} \cdots \underset{}{\overset{\|\|}{N}}$, which is not meant to imply any kind of bond between the aromatic residue and the nitrogen, but only that there is an interaction between the unsaturated nucleus and the unsaturated nitrogen which increases stability and is only possible in the aromatic series. Such ideas we shall see elaborated in the work on colour.

The allocation of the " *syn* "-configuration to the normal, unstable and reactive compounds, and of the " *anti* " to the stable *iso*-series rests mainly on the Wislicenus principle and on the view that the *syn*-compounds would have a larger energy content and so be more reactive. Since only the " normal " compounds undergo the reaction $Ar{-}N_2{-}X \longrightarrow ArX + N_2$ and only suitably substituted " normal " compounds undergo ring closure, *e.g.*,



the " *syn* "-configuration for the normal series appears to follow. But in view of Meisenheimer's work on oximes these arguments can no longer be regarded as decisive. It is, however, interesting to note that the " *anti* "-configuration of azobenzene, which, on Hantzsch's view is indicated by its stability, is established by the zero value of its electric moment.

Hantzsch completed his work on tervalent nitrogen by the investigation of the extremely unstable aliphatic diazo-compounds, and other related compounds such as hyponitrous acid and hydrazoic acid, in which he obtained results of much practical importance without any enlargement of general theory.

Pseudo-acids and -bases.

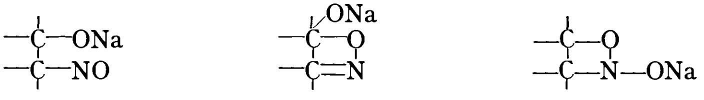
The investigation of changes in constitution during the formation of salts from tautomeric substances had formed an important part of the work on diazo-compounds. In 1894 Nef advanced the formula $R\cdot CH{=}N\!\lessdot\!{}^{O}_{ONa}$ for the salts of nitromethane and nitroethane, and in 1895 Holleman had shown that the yellow solution of *m*-nitrophenylnitromethane on acidification with hydrochloric acid retains for a time its yellow colour and shows an electrical conductivity greater than that of the sodium chloride in it, but that the colour and excess conductivity gradually disappear. Hantzsch in 1896 isolated acidic forms of phenylnitromethane and *p*-bromophenylnitromethane, of which the former was independently obtained by Holleman.

In 1899 Hantzsch published a paper dealing in a general way with the experimental characteristics of salt formation involving constitutional change. Of these the most important are: (*a*) abnormal neutralisation phenomena, *i.e.*, formation of a neutral substance by the action of an acid on a salt, or of a salt by the action of an alkali on a neutral substance; (*b*) the existence of a time factor in the processes mentioned in (*a*); (*c*) a change of colour on salt formation or the reverse; (*d*) a degree of hydrolysis of a salt less than that corresponding to the acidic properties of the substance from which it is derived—called " abnormal " hydrolysis; and (*e*) absence of normal chemical reactions, *e.g.*, the absence of reactions with phosphorus pentachloride, phenyl *iso*cyanate, and dry ammonia for substances which nevertheless give salts. Other methods were given, but these, like the chemical methods quoted under (*e*), were found in the course of the next few years to have no general validity, though of value since a result indicated by several of them could be accepted. The neutral substances which nevertheless formed salts Hantzsch called pseudo-acids, and corresponding criteria for pseudo-bases were formulated later.

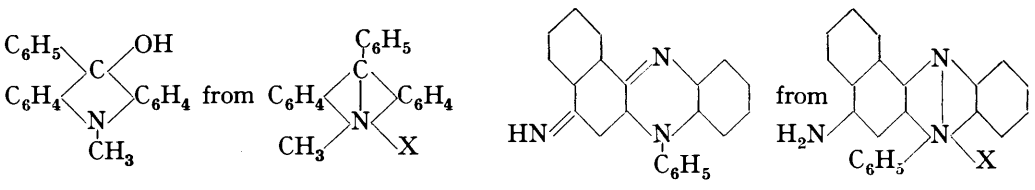
In 1904, contemporary chemists, who had accepted " abnormal " hydrolysis without question as a necessary consequence of the existence of an acid and a neutral form, were greatly surprised by H. Kauffmann's proof that it was incompatible with the law of mass action. The work of Ley and Hantzsch in 1906 showed that the difficulties of determining accurately the dissociation constants of pseudo-acids and the hydrolysis of their salts had not been sufficiently realised in the earlier work, and confirmed experimentally the conclusions of Kauffmann. Thus the most important tests for pseudo-acids (and bases) were the first three, and of the experimental methods for applying the first two, measurement of electrical conductivity proved most certain, particularly in the form originally used by Holleman, where the conductivity of a solution of equivalent amounts of the salt and a strong acid is taken immediately after mixing. For, if the change of true acid to pseudo-acid is immediate, the value found is that of the inorganic salt present; if it is not immediate, the conductivity sinks gradually to this value. This method has the advantage of giving information as to the strength of the pseudo-acid (or base) unless the intramolecular change is very quick.

In this way Hantzsch showed that the true acids corresponding to pseudo-acids are often much stronger than the ordinary organic acids, and that the true bases methylquinolinium hydroxide, phenylmethylacridinium hydroxide, and many of the bases of the di- and tri-phenylmethane dyes are, at the moment of their formation, very strongly ionised. At varying rates these coloured ionised bases change into colourless non-ionised carbinols, the rate of change being proportional to the product of the concentrations of the coloured ion and the hydroxyl ion, as it should be on Hantzsch's interpretation. The constitutional change which occurs when true bases change to pseudo-bases was found to occur also when the hydroxyl is replaced by certain other groups. In all cases it occurs with the cyanides and in the acridinium series it occurs also with the thiol and the phenylthio-group (SH and $S{\cdot}C_6H_5$). The true bases were investigated at this time only in solution, but later a coloured base, which gave a coloured salt immediately, and a colourless base, which gave the coloured salt only slowly, were isolated from hexamethyltriaminodiphenylnaphthyl chloride by Noelting—a result comparable with the isolation of two forms of phenylnitromethane.

In many cases where Hantzsch proved the existence of pseudo-acids or -bases, two alternative formulæ for the compounds had already been under discussion, and the advance he made was the demonstration of the existence of both forms and the determination of the condition of stability for each—a matter of primary importance in the interpretation of their reactions. But in some cases he found changes in constitution unsuspected until then, and proposed new formulæ, with little supporting evidence. Thus for the salts of *iso*nitroso-ketones he suggested at first the three alternatives :—



In the aromatic series a coloured form was always given a quinonoid formula. Thus the nearly colourless base from phenylmethylacridinium salts was formulated as a carbinol, but the coloured bases from the azine dyes as quinoneimines :—



Hantzsch's formulæ received much criticism. He had little difficulty in disposing of the suggestion of v. Baeyer and Villiger that what he had described as the " true " bases of the triphenylmethane series were in reality Homolka bases, but though he advanced powerful general arguments against the carbonium bond theory of the same authors (1905)—according to which the slow colour change for, *e.g.*, fuchsine was formulated

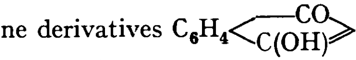
$$(NH_2{\cdot}C_6H_4)_3C{\sim\sim}OH \longrightarrow (NH_2{\cdot}C_6H_4)_3C{\cdot}OH$$

where the wavy line indicates a carbonium bond, responsible both for colour and for conductivity, this type of formulation survived for some compounds for many years. His formulation of the dyes of the oxazine and thiazine series as ammonium salts led to a controversy (1905) with Kehrmann, A. G. Green, and others who preferred to formulate them as oxonium and thiazonium salts. In the end he admitted the possibility of the latter formulation for compounds of these series, but regarded it as improbable when the molecule contains an amino- or alkylamino-group.

Colour and Absorption Spectra.

The paper on coloured *aci*-nitro-ethers in 1906 may be regarded as the starting point of Hantzsch's investigation of the problems of auxochromic action and colour. In his work on pseudo-acids Hantzsch had taken it as axiomatic that a change of colour which accompanies an apparently simple reaction such as salt formation or esterification is a certain sign that the reaction is not in reality simple but has involved a change of constitution. Similarly, having shown that unsubstituted aromatic nitro-compounds are colourless, and that the substitution of groups not subject to constitutional change in the nitro-compound does not produce colour, he attributed the production of colour by auxochromic groups to the formation of a quinonoid form. Thus trinitroanisole and *o*-nitroanisole show no absorption bands, while the absorption spectra of the two corresponding coloured *aci*-ethers are practically identical and resemble those of the sodium salts of the corresponding nitrophenols. In the case of 2 : 4-dinitrophenol the light absorption of its solution runs parallel with its conductivity, which shows that the colour is due to the presence of a strongly acid *aci*-form. The coloured solid nitro-compounds, much less intensely coloured than their sodium salts, were assumed to be solid solutions of the *aci*-form in the colourless true nitrophenols. Since *m*-nitrophenols are themselves coloured and give coloured salts, Hantzsch felt bound to accept a quinonoid form for these also, even though no *m*-*aci*-ethers had been obtained and the existence of *m*-quinones was regarded as exceedingly improbable.

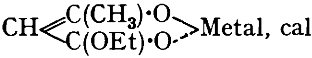
These views were opposed by Kauffmann, who maintained that change of colour could occur without change of constitution, being due then to a change in the condition of the aromatic ring which could not be expressed in terms of ordinary valency and probably involved the sub-division of valency bonds. The best single example in favour of Kauffmann's view is nitroquinol dimethyl ether, which according to Hantzsch should be colourless and actually is so in hexane, but is coloured in alcohol and other solvents of high dielectric constant. It thus became necessary to define with accuracy the variation which a light absorption curve might show with change of solvent, degree of ionisation, polymerisation, etc.—in other words to find the limits of applicability of the generalised form of Hantzsch's axiom, that change of absorption spectrum implied change of constitution.

By 1912, from the investigation of substances saturated with regard both to ordinary and to subsidiary valency such as the ions MnO_4', CrO_4'', $PtCl_6''$, $Fe(CN)_6'''$, and $Cu(NH_3)_4^{\cdot\cdot}$, Hantzsch found that within very wide limits of solvent and concentration, the light absorption per molecule is constant, and independent of the colourless cation or anion. In some cases, both for ions and for neutral substances, small displacements of the absorption curves were caused by change of solvent and since in other cases these are entirely absent—*e.g.*, the absorption curves of potassium permanganate in water, methyl alcohol, and concentrated sulphuric acid are identical within the limits of accurate measurement—Hantzsch assigned these slight displacements to the formation of solvates. That absorption is independent of ionisation is well shown in the case of fulminic acid, and for certain oxindone derivatives  $C_6H_4{<}\begin{matrix}CO\\C(OH)\end{matrix}{>}CR$, for in these cases the hydrogen compound, the salts with alkali metals, and the esters gave practically identical absorption curves. From this work it followed (1) that whenever a substance shows more than a trifling change in its absorption with change of concentration or solvent a chemical change must be assumed which, if the change is small, is the formation of a solvate and if large a change of constitution, and (2) that when there is more than a small change of absorption on the formation of a salt or an ester a change of constitution has occurred. All Hantzsch's subsequent work on chromoisomerism and on acids is founded on these two principles.

Hantzsch's interpretation of absorption curves also involved ideas for which less evidence could be given. Previous workers on absorption spectra had either followed Hartley in deducing similarity or difference of constitution from the resemblance or the difference of absorption curves, or, like Baly, had assigned a particular band, characterised principally by the frequency of its head and to a lesser degree by its persistence, to the occurrence of a particular atomic system in the molecule. For Hantzsch, the chief characteristic of an absorption curve was its form, and the preservation of the form of the curve through a series of compounds, even with considerable changes in its position on the frequency scale and in its persistence, was to him a proof of constant structure. Variation in persistence he attributed to changes in the position of equilibrium between two absorbing forms, and variation of the frequency of the head to secondary constitutional effects not capable of representation by ordinary structural formulæ. Only from an alteration in the form of the curve did he deduce a change of constitution in the ordinary sense.

The main general result of Hantzsch's work on absorption spectra, during which he examined hundreds of compounds, was to show that salt formation frequently produced a persistent band in the ultra-violet not given by the corresponding ester and usually not by the corresponding hydrogen compound. Thus acetoacetic ester in a number of different solvents shows general absorption intermediate between that of dimethylacetoacetic ester and ethoxycrotonic ester, which both show general absorption only—a result corresponding to the existence of the equilibrium

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et \rightleftharpoons CH_3{\cdot}C(OH){:}CH{\cdot}CO_2Et$$

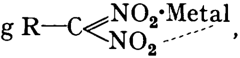
But the salts of acetoacetic ester show a deep band which is largely independent of the metal. This indicated, according to Hantzsch, the production of a new constitutional type,  $CH{<}\begin{matrix}C(CH_3){\cdot}O\\C(OEt){\cdot}O\end{matrix}{>}Metal$, called by him the conjugated *aci*-form. Here he was using a formulation previously applied by Tschugaeff in 1907 to one class of mordant dyes and by Werner in 1908 in a general theory of mordants.

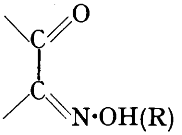
Similar evidence for the existence of conjugated *aci*-forms was found in dinitroparaffins, nitro-ketones, *iso*nitroso-ketones, nitrophenols, hydroxyazo-compounds, and in many other series where a salt-forming compound contains two reactive groups. But in addition these compounds show the phenomenon termed by Hantzsch chromoisomerism. Thus the simple aliphatic nitro-compounds give only one series of salts, but where a second nitro-group, or some other group broadly described as unsaturated, is present in the molecule in a suitable position, several series of salts distinguished by their colour may be obtained; *e.g.*,

Dinitroparaffins of type $R{\cdot}CH(NO_2)_2$ give colourless, red, and yellow salts.
Aliphatic α-nitro-ketones give colourless, red, and yellow salts.
Nitrophenols give red and yellow salts.
Dinitro-compounds of type $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}NO_2$ give colourless, yellow, red, green, and violet salts.

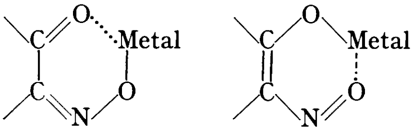
Usually each compound gives only one salt with a particular metal, but in a few cases two different salts are formed with the same metal, *e.g.*, red and yellow potassium salts of tribromo-*m*-dinitrophenol, and red and yellow thallium salts of picric acid. In almost all cases the different coloured salts dissolve in any one solvent to give identical solutions, but the colour and absorption spectra of the solutions vary with the solvent. The red and yellow potassium salts of tribromo-*m*-dinitrophenol undergo change in solution sufficiently slowly to allow it to be proved that both salts are unimolecular and ionised to the same extent. Since the colour of the solid salts is not always altered by different degrees and kind of solvation, Hantzsch argued that solvation is not the cause of the different colours in different solvents.

For aliphatic oximino-ketones and their derivatives, such as diphenylvioluric acid, similar but even more extensive ranges of salts were found, including red, orange, yellow, blue, green, and violet salts. In general, for all the compounds which show chromoisomerism, the stability of the deeper coloured salts increases with the positive nature of the metal, and the depth of colour in different solvents increases in the order phenol, chloroform, ethyl acetate, acetone, pyridine, and piperidine—*i.e.*, from acidic to basic solvents.

All the solutions of these salts show a deep band in the ultra-violet, characteristic in Hantzsch's opinion of conjugated *aci*-forms. In the case of the dinitroparaffins this is the only band, corresponding to the fact that the symmetry of the compound allows of the conjugation in only one way to produce the ring  $\mathrm{R{-}C}\Big\langle^{\mathrm{NO_2 \cdot Metal}}_{\mathrm{NO_2}}$, the variation in colour of the salts being due to slight difference in the effect of different metals, which alter the extent to which the absorption penetrates into the visible spectrum. But for unsymmetrical dinitro-compounds, the band is found to alter its position in different solvents, a change which Hantzsch attributes to the possibility of two different conjugated *aci*-forms, and the number of chromoisomerides is correspondingly increased. For substances such as oximino-ketones, which themselves might exist in two different tautomeric forms each showing its own type of absorption, Hantzsch writes the formulæ

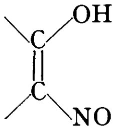


Leuco-salts.
Esters.
Free compound.



(*a*) (*b*)

Coloured salts.

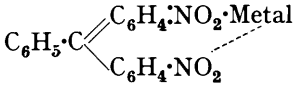


Unknown nitroso-form.

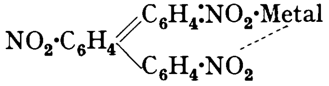
In this case the spectrum of all the salts shows the deep band in the ultra-violet corresponding to the conjugation, and a second band in the visible region variable in position and intensity, which for the blue salts resembles that of the blue nitroso-compounds and for the yellow and red salts that of true oximino-salts. Thus Hantzsch gave the yellow salts the formula (*a*) and the blue salts the formula (*b*), the intermediate colours being due not to equilibria but to alterations of the distribution of valency in the ring, giving forms which can be regarded as intermediate between (*a*) and (*b*) but cannot be formulated in any simple way. Hantzsch notes that ionisation without colour change cannot be explained on this formulation and also the further difficulty that, since in the case of the nitrophenols the absorption spectrum of the *aci*-ethers is practically identical with that of the salts, the alkyl group must be supposed to exert subsidiary valency. A further difficulty not mentioned by Hantzsch lies in the fact that salts with amines show chromoisomerism in no way different from those of the alkali metals, so that quinquevalent nitrogen also must be supposed to exert subsidiary valency.

The results obtained with many groups of coloured substances were formulated on similar lines, but Hantzsch's views on the actual significance of conjugation gradually changed. The conjugation in chromoisomeric salts was attributed to the operation of partial valencies in a manner already made familiar by Werner's work. But in other cases, *e.g.*, salts of hydroxyazo-compounds, aminoazo-compounds, and polynuclear nitro-compounds and the di- and tri-phenylmethane dyes, Hantzsch found in the absorption spectra evidence for conjugation which could only be expressed in formulæ by supposing that some kind of interaction took place between groups which were very far apart in the molecule and not otherwise known to possess partial valency. Thus the alkali-metal salts of mononitrotriphenylmethane give a band resembling that of quinone and quite different from the much greater absorption shown by the salts of di- and tri-nitrotriphenylmethane, and Hantzsch formulated these compounds :

$$(C_6H_5)_2C{:}C_6H_4{:}NO_2\cdot Metal$$



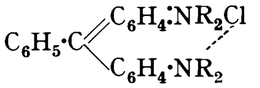
$$C_6H_5\cdot C\left\langle\begin{matrix}C_6H_4{:}NO_2\cdot Metal\\ C_6H_4\cdot NO_2\end{matrix}\right.$$



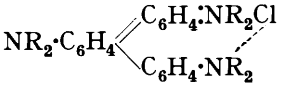
$$NO_2\cdot C_6H_4\cdot C\left\langle\begin{matrix}C_6H_4{:}NO_2\cdot Metal\\ C_6H_4\cdot NO_2\end{matrix}\right.$$

It is to be noted that the third nitro-group produced very little change in the absorption; so the very great change in absorption in passing from the mono- to the di-nitro-compound must involve the formation of a new constitutional type in which salt formation involves two nitro-groups as expressed in these formulæ. For similar reasons the salts of the aminotriphenylmethanes were formulated :

$$(C_6H_5)_2C{:}C_6H_4{:}NR_2$$



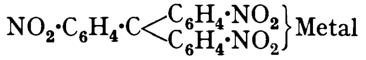
$$C_6H_5\cdot C\left\langle\begin{matrix}C_6H_4{:}NR_2Cl\\ C_6H_4\cdot NR_2\end{matrix}\right.$$



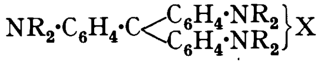
$$NR_2\cdot C_6H_4\cdot C\left\langle\begin{matrix}C_6H_4{:}NR_2Cl\\ C_6H_4\cdot NR_2\end{matrix}\right.$$

In both sets of formulæ groups very far apart in the molecule are shown as directly affecting one another; in the second set the formulæ depend on the existence of salts in the undissociated state, and express conjugation between halogen and tervalent nitrogen for which there is no analogy in other work on partial valency.

By 1919, Hantzsch's view of conjugation was radically different from the one he had originally held. Referring to the two sets of formulæ just given, he wrote : " The difference between the quinonoid and the non-quinonoid part of the conjugated complex, expressed in these formulæ, does not really exist, for in every other way there is identity. The formulæ can be simplified to



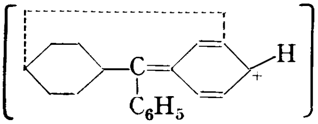
$$NO_2\cdot C_6H_4\cdot C\left\langle\begin{matrix}C_6H_4\cdot NO_2\\ C_6H_4\cdot NO_2\end{matrix}\right\}Metal$$



$$NR_2\cdot C_6H_4\cdot C\left\langle\begin{matrix}C_6H_4\cdot NR_2\\ C_6H_4\cdot NR_2\end{matrix}\right\}X$$

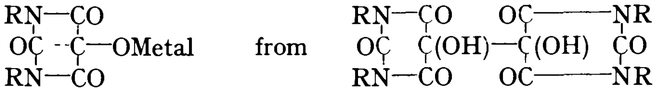
but these omit altogether the quinonoid character, which is essential. Again, the third NO_2 or NR_2 is not totally unaltered or excluded from the conjugation, but at any point of time only two of the nitro-groups or two of the amino-groups are taking part in the binding of the metallic or acidic ions. Thus the simplest formulæ are $C(C_6H_4NO_2)_3Metal$ and $C(C_6H_4\cdot NR_2)_3X$, but this simplification must be taken as giving incomplete formulæ." This passage makes it perfectly clear that Hantzsch no longer regarded conjugation as expressible by static formulæ involving partial valency, nor even as an equilibrium between various forms which could each be given a static formula, but as a state of the molecule, dependent on all its parts and requiring for its existence certain structural features.

Some of these features had been recognised by previous workers on colour, for v. Baeyer many years previously had attributed the colour of the triphenylmethane dyes to a " rhythmic vibrational effect " and Pfeiffer had advanced the *meri*-quinonoid theory. Hantzsch's view may be said to include and supersede both these ideas, and it comes very near indeed to the most recent views on the subject. We know now that the positive ion of a di- or a tri-phenylmethane dye will not actually exist in the ordinary quinonoid form, for since only electronic displacements are involved when two of the aromatic nuclei interchange their quinonoid and benzenoid functions, resonance must occur, and the ion will exist in an intermediate form of lower energy content, not expressible by ordinary structural formulæ. The inorganic ion will not be involved in the resonance, but since it is the organic ion which shows resonance, the presence of an ion of opposite sign is involved and this explains the necessity, which Hantzsch felt, of assigning a definite function to this ion. In the great majority of cases where Hantzsch wrote conjugation formulæ, we know now that resonance will occur. In conjugation he recognised clearly the existence of a new constitutional effect, and he realised experimentally some of the consequences of resonance long before its occurrence was deduced theoretically. That he should have been unable, as indeed we are to-day, to express ideas on this subject in terms of the conventional system of notation is less remarkable than his clear recognition of an unsuspected structural state. But because Hantzsch's ideas went beyond the classical theory of structure, they were received rather as interesting speculations than as constituting a fundamental advance in molecular theory.

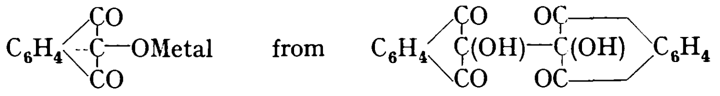
The theory advanced to explain the colour of derivatives of triphenylmethane, according to which the deep colour of dyes is characteristic of molecules which cannot be represented by a static formula, but which may be regarded as containing a quinonoid part and a non-quinonoid part between which there is the relation which Hantzsch calls conjugation, can be applied satisfactorily to many other series, including the acridine, pyronine, azine, oxazine, thiazine, and azo-dyes. The colour of such substances as triphenylmethyl chloride he thought to be due to the presence of a form having the same constitutional features as the dyes but containing the carbonium ion. Thus $(C_6H_5)_3CCl$ is colourless and in terms of his later nomenclature is a pseudo-salt, which changes over partly in certain solvents to the true salt,  $\bar{C}l$, for he found that the colour and electrical conductivity of triphenylmethyl chloride in different solvents varied together. On the other hand, he ascribed the halochromy of dibenzylideneacetone and the simple ketones to the formation of simple carbonium salts, *e.g.*, for benzophenone in sulphuric acid to the presence of

$$[HO\cdot C(C_6H_5)_2]^+HSO_4^-$$

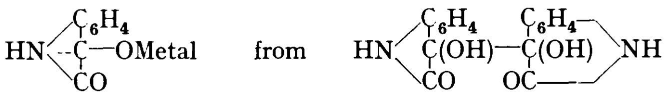
and in the case of the intensely blue salts of alloxantin, hydrindantin, and isatide, which chemically have considerable resemblance to the blue metal ketyls of Schlenk, he thought the colour to be due to the extreme unsaturation of uncharged tervalent carbon, thus:



Alloxantin.

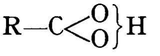


Hydrindantin.



Isatide.

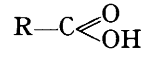
In 1917 his last great research began with a paper on the ultra-violet absorption spectra of carboxylic acids and their salts and esters. Using accurate spectroscopic methods, he found that, whereas all the alkali salts of a particular acid are optically identical, and all the esters are optically identical, the two classes do not give the same absorption. The acids themselves show varying absorption, which is intermediate between that of the salts and the esters when they are examined in the pure state or dissolved in water or light petroleum, but identical with that of the esters when dissolved in alcohol or ether. Since light petroleum acts simply as a diluent, solutions in it give the same absorption spectra as the pure acids, which in general are different from those of aqueous solutions, though of the same type. But in one case—trichloroacetic acid—water and light petroleum give solutions optically identical with those of its salts in water. There is thus evidence of constitutional change in salt and ester formation, and of the existence of constitutionally different forms of the acid not explained by the usual formulæ or by ionisation. These forms Hantzsch thought to be



$$R{-}C{<}\left.\begin{matrix}O\\O\end{matrix}\right\}H$$

True acid and salt.

and



$$R{-}C\begin{matrix}\ll O\\ < OH\end{matrix}$$

Pseudo-acid and ester.

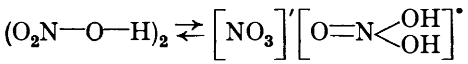
in the former of which the hydrogen atom is capable of direct ionisation, while the latter represents a pseudo-acid which is not directly ionisable, forming ions only after changing into the acidic form, with which it is normally in equilibrium. For similar reasons nitric acid was supposed by Hantzsch to exist as a true acid $[NO_3]H$ and as a pseudo-acid $O_2N{-}O{-}H$, but other strong acids he regarded at first as wholly true acids.

During the next ten years the whole range of organic and inorganic acids was investigated by means of their ultra-violet absorption spectra, molecular refractivity and electrical conductivity, by the relative stability of their salts as determined by indicator methods, by the relative stability of their compounds with water, alcohol, and ether, and by their catalytic effects on the rate of inversion of sucrose and on the rate of decomposition of diazoacetic ester. The range of solvents used was as wide as the properties of the substance and the nature of the method in use would allow, and whenever possible, the pure acids were examined in the liquid or solid state. In 1927 Hantzsch summarised his results, and put forward his final views.

The original hypothesis that some acids can exist in a true and a pseudo-form was given up in consequence of an investigation of the halogen hydrides, for Hantzsch found that in their physical and especially in their optical properties these acids are the inorganic analogues of their esters, the alkyl halides, and that they become optically identical with their alkali and ammonium salts only in aqueous solution, though approaching them in alcoholic and to a small extent in ethereal solution. Hantzsch explained these results by supposing that the halogen hydrides are pseudo-acids and that they can only ionise by reaction with a suitable solvent, forming with water a hydroxonium salt $[H_3O]X$ similar to an ammonium salt $[H_4N]X$, with alcohol the salt $[EtH_2O]X$, and with ether the salt $[Et_2HO]X$, the degree of ionisation depending wholly on the extent to which these salts are formed.

This work made it seem probable to Hantzsch that all acids might be pseudo-acids, and an examination of many acids of the types XOH, XO_2H, XO_3H, and XO_4H confirmed this view. Thus the sulphonic acids, like hydrobromic acid, give a salt-like absorption in ether and are supposed to be present as hydroxonium salts $R{\cdot}SO_3[HO(C_2H_5)_2]$. They cannot be true acids, since in indifferent solvents like chloroform they do not give salt-like absorption and their strong association in such solvents indicates the presence of a true hydroxyl group, *i.e.*, they are to be formulated as $R{\cdot}SO_2{\cdot}OH$, not as $[RSO_3]H$. A similar argument from association applies to iodic and metaphosphoric acids. There is no optical evidence for acids of the type XO_4H, for the only example suitable for investigation, perchloric acid, is optically transparent. But the high boiling point of the pure acid, indicating association, and the solubility of silver perchlorate in ether, benzene, etc., which indicates a non-polar structure of this salt, led Hantzsch to conclude that it must be formulated $O_3Cl{\cdot}OH$. In fact, according to Hantzsch, " for the existence of free true acids there is no single favourable observation."

The often very considerable electrical conductivity of pure acids, originally quoted as evidence for the existence of an equilibrium between pseudo and true acidic forms, Hantzsch finally regarded as due to the formation of " acidium " salts from two (or more) molecules of the " pseudo " acid. Thus nitric acid, itself bimolecular, he believed to form " nitracidium nitrate,"



$$(O_2N{-}O{-}H)_2 \rightleftarrows \left[NO_3\right]' \left[O{=}N{<}{}^{OH}_{OH}\right]^{\cdot}$$

which confers conductivity on the pure acid and accounts also for certain features of the absorption spectrum. Similarly in sulphuric acid, the salts $[SO_3{\cdot}OH]'[OS(OH)_3]^{\cdot}$ and $[SO_3{\cdot}OH]_2'[S(OH)_4]^{\cdot\cdot}$ were supposed to be present.

The case for the existence of such " acidium " salts is greatly strengthened by the isolation of salts formed from two separate acids. Hantzsch isolated the following compounds: $[ON(OH)_2]^{\cdot}[ClO_4]'$, $[N(OH)_3]^{\cdot\cdot}[ClO_4]_2'$, $[FH_2]^{\cdot}[ClO_4]'$, $[FH_2]^{\cdot}[BF_4]'$, $[C_2H_5O_2]^{\cdot}[HSO_4]'$, and $[C_2H_5O_2]^{\cdot}[ClO_4]'$. The first two were proved to be electrolytes in nitromethane, giving values of Λ_0 135 and 200 respectively. Analyses of the cathode liquid after electrolysis showed an excess of nitric acid which can only be explained by the presence of a cation containing HNO_3. Cryoscopic evidence of the presence of a compound of hydrofluoric acid in concentrated sulphuric acid was also obtained.

Regarding all acids as pseudo-acids, Hantzsch adopted as his criterion of acidity the relative tendency to form salts, and on this basis all the different methods he used agreed in giving the following order of acidity for monobasic acids: $ClO_4H > R{\cdot}SO_3H > R{\cdot}SeO_3H > NO_3H > CCl_3{\cdot}CO_2H > CHCl_2{\cdot}CO_2H > CH_2Cl{\cdot}CO_2H > CH_2Br{\cdot}CO_2H > CH_3{\cdot}CHBr{\cdot}CO_2H > H{\cdot}CO_2H > CH_3{\cdot}CO_2H > CH_3{\cdot}CH_2{\cdot}CO_2H > Cl{\cdot}OH$.

With water, acids give hydroxonium salts to an extent depending on their acidity, and the equilibrium reached, $XH + H_2O \rightleftarrows [X][H_3O]$, which can be determined by conductivity, is for a weak acid a measure of its salt-forming tendency. Thus Hantzsch's order for weak acids is the same as that found by the conductivity method. But for acids above a certain strength, the salt-forming tendency is enough to ensure that the acid goes over wholly into the hydroxonium salt, except in the most concentrated solutions, so that they all appear to be equally strong. Water thus produces a " levelling " effect, but in other solvents differences persist which can be demonstrated by appropriate methods.

It follows from the non-existence of true acids that, on salt formation, only metals more positive than hydrogen can give " true " salts, *e.g.*, $[ClO_4]'K^{\cdot}$, while other metals must give pseudo-salts, *e.g.*, $O_3Cl{-}O{-}Ag$, a view confirmed by refractometric measurements and solubility relations. The true salts Hantzsch thought to exist in aqueous solutions as " aquo " salts, *e.g.*, $[\text{Metal}\ (H_2O)_n]X$. The stability of pseudo-salts varies greatly; thus mercuric chloride and cupric chloride are not decomposed by concentrated sulphuric acid, and others such as aluminium salts go over in water immediately to true "aquo" salts. Pseudo-salts are often soluble in organic media, as in the case of silver perchlorate and many of the ferric compounds derived from phenolic and enolic substances. Only in one case—mercuric cyanurate—has a salt been isolated in both " pseudo " and " true " forms.

These views have been adversely criticised on the ground that the results from measurements of absorption spectra and refractive powers can be satisfactorily interpreted by the deformation theory of Fajans and the ionic association hypothesis of Bjerrum, which also explain the effects of the presence of other salts and the effects of different solvents on the absorption spectra of nitrates—effects of which Hantzsch took no account. On the other hand, the idea that nearly all oxygen compounds can act as bases, which Hantzsch first put forward in 1908 in connexion with his work on concentrated sulphuric acid and elaborated in his later work, is in agreement with the Brönsted–Lowry theory of acids, and the most recent work indicates that a quantitative interpretation of the properties of acids in different solvents follows from the recognition that the process of ionisation of acids involves reaction with the solvent.

This review of Hantzsch's chief researches can give only an indication of the magnitude of his contribution to chemistry, and though the inclusion of some of the many other important researches described in his 450 memoirs would add detail, the picture would still be incomplete. For Hantzsch was a living force in chemistry, affecting his contemporaries not merely by the actual content of his work but by the spirit and personality which the work expressed. A man of single purpose, a chemist subtle in thought and bold in experiment, an untiring pioneer in new fields, he was a leader and a prophet in his own generation. Succeeding generations inherit much from him; long may they honour his memory.