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O X O N I U M   B A S E S

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BY

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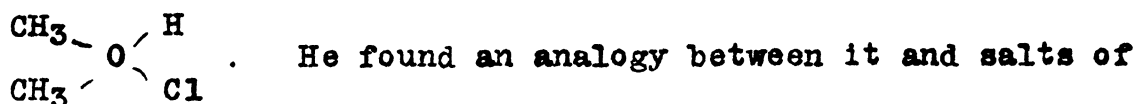
CHICAGO

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## O X O N I U M   B A S E S.

As early as 1875 Friedel obtained a compound of methyl ether and hydrochloric acid. He considered it a direct combination of these two substances and gave to it the formula



sulphonium bases such as  $(\text{CH}_3)_3\text{SI}$ . However, neither Friedel himself nor others who worked on similar substances thought of them as organic derivatives in which the oxygen might possess basic characteristics. The conscious investigation of such properties of quadrivalent oxygen did not begin until nearly twenty years later when Collie and Tickle commenced their work on the salts of dimethyl pyrone. Since then the chemistry of oxonium bases has developed rapidly and promises to add much to chemical theories and research.

The present study of the salts of oxonium bases is intended to outline the historical development of the subject, to classify the most important oxonium bases, to give the most important facts which serve as a basis for the accepted constitution of such salts, to present the physical-chemical evidence for considering them true salts, and to discuss their relation to chemical theories.

### I. HISTORY.

Friedel in 1875 (Bulletin de la Societe Chimique 24, 160) obtained a colorless, mobile liquid by passing pure and dry

methyl ether and hydrogen chloride into a vessel surrounded by a freezing mixture. By analysis he found the product which should contain (calculated for a hydro chloride  $(\text{CH}_3)_2\text{O}, \text{HCl}$ ) 42 per cent. chlorine gave from 37 to 39 per cent. of chlorine. He considered it a true compound of the two substances in which hydrogen and chlorine are bound directly to oxygen, and suggests that elements may have supplementary valences, i.e., valences which are not generally in use but are active probably only at low temperatures, the temperature varying with the substance used. He thought that  $\text{Ag}_4\text{O}$  and  $\text{Cu}_2\text{O}$  also proved the quadri-valence of oxygen and compared the hydrochloride of methyl ether with the sulphur compounds  $\text{R}_3\text{SI}$  discovered by Cahours. But Friedel himself evidently did not see the full bearing of his compound on the question of the basic properties of oxygen.

In 1876 Baeyer and Fischer (Liebig's Annalen 183, pp.27, 68) in experimenting with fluorescein and orcinphthalein discovered that by dissolving either of these substances in concentrated sulphuric acid a red syrup was formed from which yellow stable crystals were obtained. Orcinphthalein also gave red crystals with concentrated hydrochloric acid. They could not decide what constitution to give to these compounds.

About 1877 Van 't Hoff suggested (Ausichten über die Organische Chemie, p.62) that the third and fourth valences of oxygen might be positive, that is, basic. In support of this he used the fact that alcohols combine with chlorides of metals like antimony much as ammonia and amines do.

In 1879 Dale and Schorlemmer (Liebig's Annalen 196, p.84) found that aurin had only very weak acid properties and formed

unstable compounds with bases while it seemed to possess decided basic properties, forming stable, well crystallized compounds with acids. This fact is especially noteworthy as aurin is a phenol derivative containing no nitrogen but a considerable percentage of oxygen.

In 1884 Classen and Ponder (Liebig's Annalen 223, p.142) described red crystals obtained from dibenzal acetone and concentrated sulphuric and hydrochloric acids, and in 1888 Wallach (Liebig's Annalen 246, p.181) obtained a compound of with hydrochloric acid. In 1896 Perkin (Journal of the Chemical Society 69, p.1439) obtained similar compounds of quercetin and other pyrone dyes.

With the exception of Dale and Schorlemmer and possibly Van 't Hoff, all of these chemists considered these compounds either so-called "molecular combinations" or organic halogen derivatives. But in 1896 Collie and Tickle (Journal of the Chemical Society 59, p.619; 75, p.710) undertook to explain them on the basis of basic quadrivalent oxygen. In their study of the reactions of dehydracetic acid they found a crystalline product after boiling with concentrated hydrochloric acid. They thought it to be the hydrochloride of diacetyl acetone for, although a water solution behaved as a mixture of hydrochloric acid and dimethyl pyrone, it was not formed apparently by dissolving dimethyl pyrone in hydrochloric acid and evaporating the solution. Later they proved that diacetyl acetone was not present, as barium hydrate gave no characteristic yellow precipitate nor did ferric chloride give a red coloration. They also found that dimethyl pyrone dissolved in hydrochloric acid did

give the same product when treated with proper precautions to prevent loss of the acid, and that with many other acids it gave similar compounds. They thought it behaved like a salt of a strong acid and weak base, and to explain the basic properties of dimethyl pyrone made the assumption that oxygen might be quadrivalent. They suggest that as oxygen in the periodic table belongs with nitrogen, sulphur and phosphorus, all of which exhibit dual valences, it may also in favored cases have a tendency for higher valence.

The most important investigations on oxonium bases have been made by Baeyer and Villiger. They published the first results of a long series of observations in 1901 (Berichte 34, p.2679). They proved that many classes of organic compounds in which oxygen is bound to carbon are capable of forming salts of oxonium bases, the most important classes being ethers, alcohols, acids, esters, aldehydes and ketones. Among the many acids tried they found hydroferro and ferricyanic and chlorplatinic acids to give the best crystallized and least soluble salts with oxygen bases. Investigation and comparison of carbonium and oxonium salts followed from their earlier work and although questions concerning these salts have not all been answered, much light has been thrown on the subject by their experiments. Kehrman, Werner, and Hewitt have also been prominent investigators of certain classes of oxonium bases belonging to the organic dyes.

The physico-chemical behavior of these salts has been studied by Coehn, Walden, Walker and Sack , who have all contributed valuable facts concerning them.

## II. CLASSES AND PROPERTIES OF OXONIUM BASES AND SALTS.

1. Derivatives of Ether.--Baeyer and Villiger considered ethers to be the best oxygen organic compounds from which to obtain salts of oxonium bases, because they formed more stable and characteristic salts than any other classes with which they experimented, although they thought that practically every organic compound in which oxygen was bound to carbon has some tendency to combine with acids to give salts. The number and kind of carbon radicles attached to oxygen influence the ease with which oxonium compounds are formed and their stability.

Of the ether derivatives the first described is that obtained by Friedel (Bulletin de la Societe Chimique 24, 160) by the combination of methyl ether and hydrogen chloride at 0°. It is a colorless liquid, fuming in the air and boiling at -2° with decomposition.

Baeyer (Berichte 34, p.2688) obtained with diethyl ether and hydroferrocyanic acid white crystals which he was not able to analyse. These had always been considered hydroferrocyanic acid in the old qualitative test for ferrocyanides with ether and hydrochloric acid. But Baeyer showed they contained both ether and hydroferrocyanic acid. With hydroferricyanic acid he got a brown oil which gave brown needles on evaporation, and hydrocobalticyanic acid gave similar colorless needles with ethyl ether. Diisomyloether gave no compounds with ferrocyanic acid, but ferricyanic acid gave an unstable compound while hydrocobalti cyanic acid gave a well crystallized substance which was analysed and showed the composition

$(C_5H_{11})_2O, H_3CO(Cn)_6 + 2H_2O$ . Anisol with ferricyanic acid and

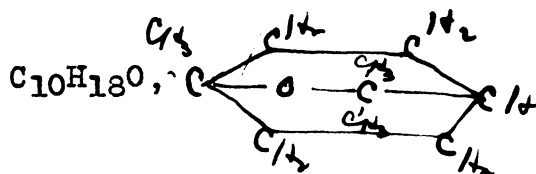


paraldehyde with ferrocyanic acid gave large crystals. It is interesting to note that the salts of anisol derivatives belong to this class as salts of phenyl ethers, because they are so important as material for the theory of color in organic bodies, as will be discussed in Part V.

The pyrones are interesting members of this class, as they contain both an ether and a carbonyl oxygen atom. Baeyer, who experimented with dimethyl pyrone, proved that it is a diacid base, each oxygen atom being capable of taking up a molecule of acid. The compound containing one acid molecule is the more stable, but it is hard to determine whether the ether oxygen or the carbonyl oxygen holds the acid. On the one hand, unsaturated organic compounds such as aldehydes, ketones and quinoid derivatives form oxonium salts with readiness. On the other hand, the most stable oxonium salts discovered seem to be those of cineol, which is an intramolecular ether. The latter fact led Baeyer to the conclusion that the mono acid salts of pyrene are probably oxonium salts of the ether oxygen atom. Collie and Tickle (Journal of the Chemical Society 75, p.710) prepared and described several of these salts of dimethyl pyrone. Beside the hydrochloride crystallizing in transparent plates and melting at 84-85°, they obtained the hydrobromide, hydriodide, platino chloride, nitrate, oxalate, tartrate, chloracetate, salicylate, and picrate. These all are well crystallized salts which on analysis give very nearly the required percentage of acid. All the salts are neutral,  $C_7H_8O_2, HX$ , except an acid oxalate and an acid tartrate  $C_7H_8O_2, H_2X$ .

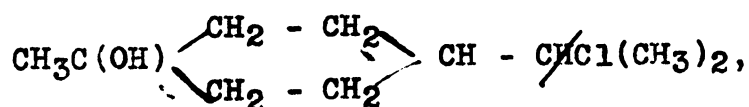
The salts obtained from cineol also belong to this class of ether salts.

Cineol,  $C_{15}H_{26}O$



is known also as eucal-

yp<sub>1</sub>tol. Wallach (Liebig's Annalen 246, p.280) described crystals of the hydrochlorid,  $(C_{10}H_{18}O) HCl$  (?) (see Part IV), and the better defined hydrobromide,  $(C_{10}H_{18}O)HBr$ . These cineol salts are interesting because Sacken in his experiments on the physico-chemical behavior of oxonium bases used them on account of their comparative stability. The fact that the acid in these salts is split off instantly by water proves that they are true salts of a very weak base and not the isomeric addition products, such as

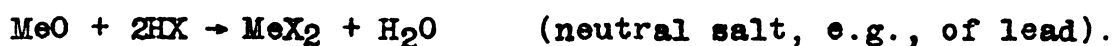
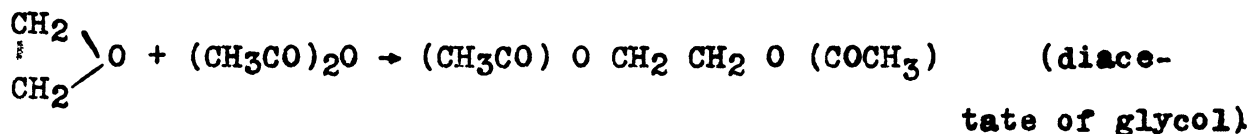


no true chlorhydrin being known which loses its acid so easily.

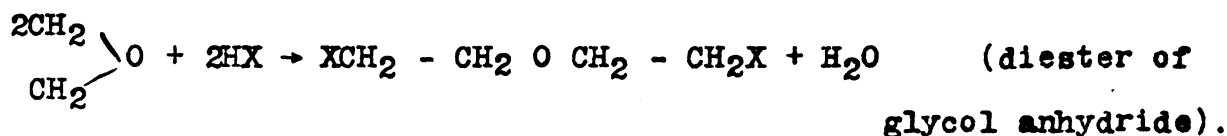
Another class of intramolecular ethers of interest for the oxonium theory is that of ethylene oxide and its alkyl derivatives. The basic properties of these compounds have long been a subject of discussion and experiment. Wurtz, who discovered ethylene oxide (Annales de Chimie et de Physique 69, p. 355) compared it and its derivatives with metal oxides, as he found an analogy between the molecular formulae of metal oxides and their basic and neutral salts, and the molecular formulae of ethylene oxide and the glycol and diethylene oxide esters which are easily formed by the absorption of acids. That these esters were true salts of ethylene oxide was his conception, although it does not agree with the modern idea of salts. As evidence of the parallelism between ethylene oxide and metal oxides such reactions were used



and



and



These esters in many cases are formed very easily with evolution of heat on mixing the oxide with concentrated acids. The theories of modern physical chemistry will hardly allow these esters of glycol and its anhydride to be called real salts of ethylene oxide, as it has not yet been shown that they can ionize at all. However, some salts of metal oxides and acid, such as mercuric chloride and cyanide or chromic chloride, do not ionize readily and perhaps the dissociation of various classes of esters and salts may differ not so much in kind as in degree.

At present experimental justification for considering these esters to be true salts is lacking and the formation of glycol esters from ethylene oxide cannot be held as proof of its basic character. It shows merely the instability of the triatomic ring which can open to give  $\begin{array}{c} \text{CH}_2 - \text{O} - \\ | \\ \text{CH}_2 - \end{array}$  and this unsaturated group can then absorb an acid, amine or aldehyde.

Wurtz used as a second proof of the pronounced basic character of ethylene oxide the fact that it can precipitate difficultly soluble metal hydroxides from water solutions. Magnesium, aluminium, copper, ferric hydroxides are precipitated from solutions of their chlorides, with the formation of glycol chlorhydrine. But ethylene oxide can at most be but a very weak base, as it has but minimal conductivity and neutral reaction. The precipitation of difficultly soluble metal hydroxides from solutions of chlorides which are hydrolysed by water is explained by the great power of ethylene oxide to absorb acid. In a hydrolysed solution of aluminium chloride there is a condition of equilibrium according to the equation

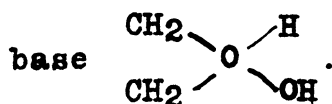


But if any agent removes the acid the condition of equilibrium is disturbed so that more hydroxide is produced until its complete precipitation follows if it is difficultly soluble. It is for this purpose that precipitated barium carbonate is used in qualitative analysis to effect the precipitation of alumina, ferric hydrate, etc. In the case of ethylene oxide and metal chlorides, ethylene oxide absorbs the hydrochloric acid as it is formed and so allows the precipitation of the metal hydroxide to go on to completion. As the formation of glycol chlorhydrin in the presence of very dilute acid is not instantaneous, the absorption of acid is slow and in the case of magnesium chloride, which is very little hydrolysed by water, the precipitation of magnesium hydroxide is effected only after twenty-four hours standing (Walker, Berichte 34, 4115). These experiments show that the reactions described by Wurtz as proof

of the decided basic properties of ethylene oxide are not due to its basic character and that at most it can be but a very weak base. When Collie and Tickle contributed their work on quadrivalent oxygen it was thought that the reactions of ethylene oxide might be explained by the presence of oxonium bases. But the formation of glycol esters in such reactions seem to prove rather the unsaturated condition of the triatomic ring

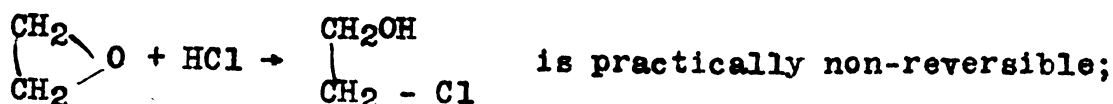
than the formation of an oxonium base  $\begin{array}{c} \text{CH}_2 \diagup \text{O} \diagdown \text{H} \\ | \quad \quad \quad \diagdown \\ \text{CH}_2 \diagdown \quad \quad \text{OH} \end{array}$ . Comparison

of ethylene oxide with dimethyl ether and cineol indicate that ethylene oxide ought to be able to form an oxonium base and salts, and the fact that its aqueous solution does have a minimal conductivity, due to the formation of some hydroxyl and oxonium ions, seems to sustain these comparisons. Baeyer (Berichte 34, p.2689) obtained a precipitate when hydroferrocyanic acid was treated with ethylene oxide in a freezing mixture. He thought it might be a ferrocyanide or possibly a hydrate, but does not seem to have carried out any further work with it. Wurtz (Annales de Chemie 69, p.318) described crystals obtained by mixing ethylene oxide and water at  $0^\circ$ . They were fairly stable at that temperature and he proved that they were not ice or glycol, which is an oil at that temperature. He thought they were probably crystals of an unstable hydrate of ethylene oxide. They cannot be a cryohydrate, as they are formed at  $0^\circ$ , and so the water must be present in them either as water of crystallization or they must be the real



Ethyl ether forms a similar compound with water. Tauret (Bulletin de la Societe Chimique 30, p.505) found that the crystals which are formed on the edges of the paper when cold ether is filtered in the air have approximately the composition  $(C_2H_5)_2O, 2H_2O$ . They are not stable above  $-3.5^\circ$  and are most likely a hydrate of ethyl ether. A cryohydrate under such circumstances would require that two parts of ether be soluble in one part of water, while ether really is very much less soluble. The two molecules of water must be present combined with the ether either as water of crystallization or be accounted for in the constitution.<sup>1</sup>

If ethylene oxide does form an oxonium base and salts as these facts suggest, then there must be a series of true salts corresponding to, and isomers of, the esters of glycol which Wurtz thought were salts of ethylene oxide. Such salts would be easily hydrolysed as salts of a very weak base and would therefore go over into the more stable esters of glycol.



so that equilibrium is established only when practically all the ethylene oxide has been converted into the more stable glycol chlorhydrin.

2. Alcohols.--That alcohols might have basic characteristics due not to dissociation into hydroxyl ions and alkyls but to extra valences of oxygen which change the properties of the alcohols, was first suggested by Van 't Hoff. As support of his

1. Ethers combined with more than one molecule of a haloid acid, such as were obtained by Walker and McIntosh, will be discussed in Part IV.

opinion he cited the similarity of the compounds of alcohols with metal chlorides such as antimony chloride, to those formed by amines and ammonia. He described analogous compounds of sulphur--the *mercaptans*--which by treatment with alkyl halides give salts  $R_3SX$  in which the valence of sulphur certainly changed, involving a change of properties (Ausichten über die Organischen Chemie, p.62).

Some salts of alcohols are described by Baeyer (Berichte 34, 2690). With primary alcohols he describes the compound of amyl alcohol and hydroferricyanic acid; with secondary alcohols, compounds of menthol, borneol, tetrahydrocarveol, and hydroferricyanic acid; with tertiary alcohols the compounds of trimethyl carbinol and hydroferrocyanic acid.

3. Derivatives of Esters.--Baeyer (Berichte 34, 2692) prepared various salts of esters. He found that hydroferricyanic acid gives crystalline compounds with esters of acetic acid, with the ethyl esters of benzoic and oxalic acids and the amyl ester of valerianic acid. Hydroferrocyanic acid gave no compounds with esters of benzoic or acetic acid, but gave the best and most stable compound of this whole group with ethyl oxalate. This salt on analysis had the composition  $C_6H_{10}O_4, H_4Fe(CN)_6$ .

It is possible that the formation of such salts explains the catalytic action of acids in hydrolysing esters.

4. Derivatives of Acids.--Acids apparently do not form oxonium salts readily. But Baeyer placed in this class the perbromide of the hydrobromide of acetic acid obtained by Steiner (Berichte 7, p.184) having the composition

$(C_2H_4O_2)_2HBr, Br_2$ . Rosenheim has done the most important work on the basic character of acids (Berichte 34, p.3377; 35, p.1115). He obtained combinations of organic acids with antimony tri- and pentachlorides which were similar in every respect to those obtained with esters of acids and antimony chlorides. From this fact he concluded that the acids must have basic properties as well as the esters. In the same way Van 't Hoff had concluded that alcohols could have basic properties because they united with antimony chlorides just as ammonia and amines do.

5. Derivatives of Aldehydes.--Many crystalline salts of aldehydes were prepared by Baeyer (Berichte 34, p.2692). Benzaldehyde gave compounds with hydro cobalti cyanic, hydro ferro cyanic, and hydroferricyanic acids. The last were deep-orange in color. Cinnamic aldehyde also forms interesting compounds with these reagents, and beautiful orange-red crystals with hydrochloroplatinic acid. The nitrate of cinnamic aldehyde is perhaps the best and longest known of the salts of oxygen derivatives. Its preparation is described by Dumas and Pelifot (Liebig's Annalen 14 (1835), p.61). The ease with which it is formed seems to indicate that the double bond near the oxygen intensifies its basic characteristics in a marked manner. (See Part V.)

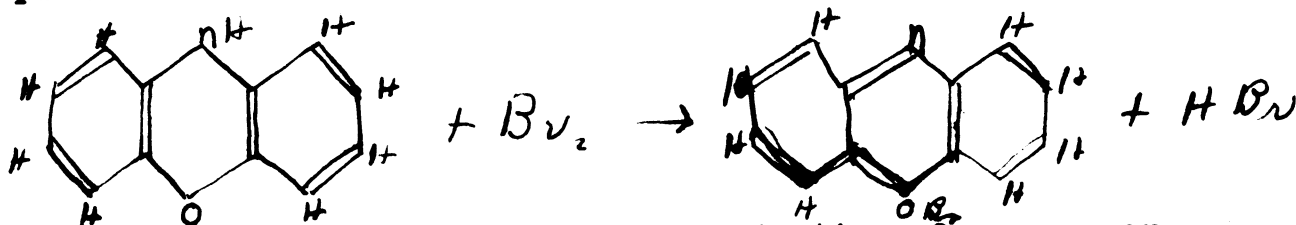
6. Derivatives of Ketones.--The ease with which ketones form salts is characteristic of this class. Among all the ketones which Baeyer tried, he found only one, benzophenone, which gave no salt. From acetone (Berichte 34, p.2693) he only succeeded in preparing double salts with cineol and hydroferri-



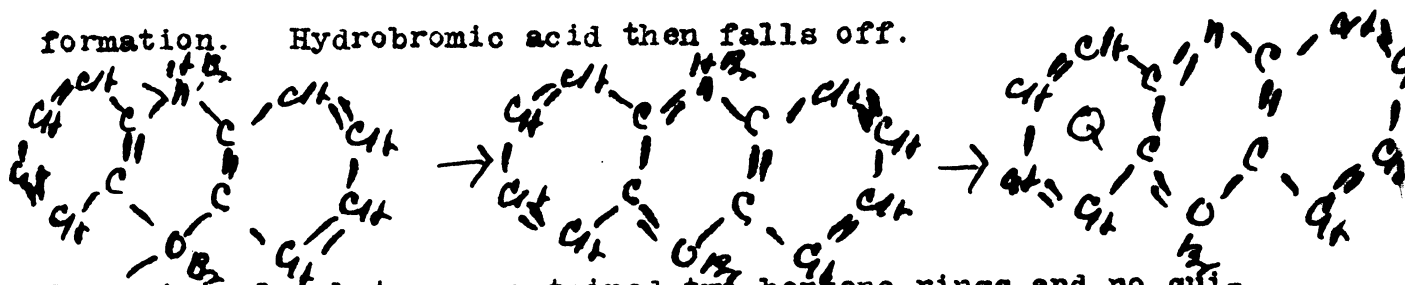
cyanic acid. He thought that their great solubility may have prevented the isolation of simple salts. All classes of ketones gave compounds with hydroferro-, hydroferri-, and hydrocobalticyanic acids. Many of them were well crystallized bodies. McIntosh, Walker and Archibald (Journal of the Chemical Society 85, p.919) using liquefied halogen acids at low temperatures with acetone obtain a hydriodide, a hydrobromide, and a hydrochloride. The quinones also belong in this class of ketones and form interesting oxonium salts. Baeyer and Villiger (Berichte 34, p.2697) describe a salt they obtained from parabenzoquinone and phosphotungstic acid. It crystallizes as bright-yellow tablets. Kehrman (Berichte 35, p.343) prepared a nitrate of phenanthrenequinone. He succeeded in crystallizing it as beautiful prisms resembling potassium bichromate. Probably the salts of methoxytriphenyl carbinol belong in the class of quinone salts. These are especially interesting as they are connected with the question of the relation of color to structure, especially in the triphenylmethane dyes. This question will be considered in Part V.

7. Azoxonium and Carboxonium Salts.--Another interesting class of oxonium salts is that in which the basic oxygen atom holds three carbon valences beside the acid radicle. In the other classes the oxygen atom holds a hydrogen and an acid radicle and so was united with only two carbon valences. Although chemists have, as yet, been unable to prepare trialkyl oxonium salts ( $R_3O$ ), corresponding to the fully alkylated ammonium salts ( $R_4N$ )X, representatives of this type are found in the azoxonium and carboxonium salts  $R = O \begin{smallmatrix} \diagup R \\ \diagdown X \end{smallmatrix}$ .

Kehrmann (Berichte 32, 2601; 34, 1623; Liebig's Annalen 322, p.1) obtained some simple azoxonium salts by oxidizing phenoxazines with bromine. The action may be represented thus:

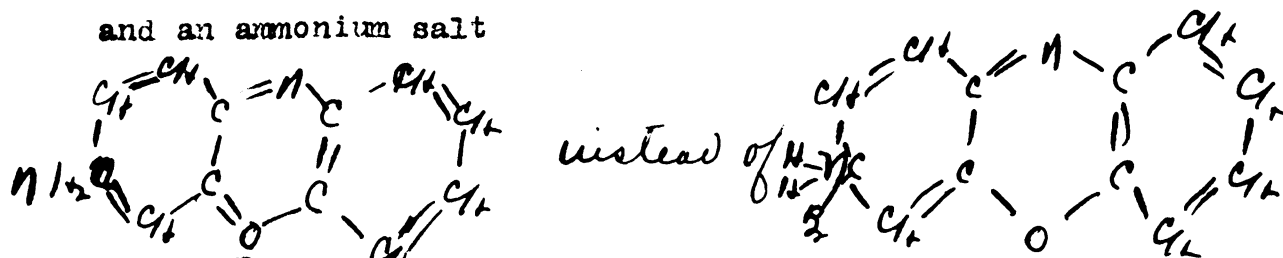


This oxidation seems similar to the oxidation of a para- or ortho- hydro quinone to a quinone. Probably the first step in the reaction is the addition of bromine atoms to the nitrogen and oxygen atoms of phenoxazine. Then the two free valences of nitrogen and oxygen open the adjacent double bonds and cause them to close in a different manner according to the quinone formation. Hydrobromic acid then falls off.

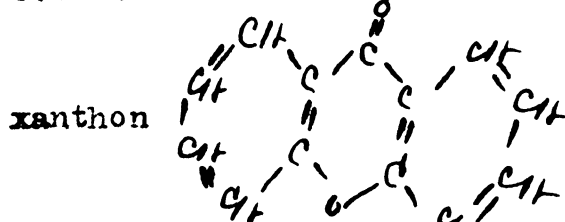


The original substance contained two benzene rings and no quinone group, while the salt is a quinone derivative, with a quinone nucleus, Q. The fact that the original substances are colorless while the derivatives are colored agrees perfectly with the quinone formation. For instance, dimethyl phenoxazine is white while the oxidation product, dimethyl phenazoxonium bromide is violet-red. These salts also absorb aniline readily, as do most quinones, most likely at a double bond of the quinone nucleus. The oxazines which are oxidation products and are valuable dyes are of the same constitution as these salts, according to Kehrmann's ideas. He believes that the monoamid derivative, like the phenazoxonium bromide, is

an orthoquinone and an oxonium salt instead of a paraquinone and an ammonium salt

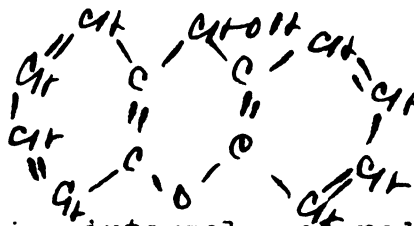


Where there might be either an ammonium or an oxonium salt it is difficult to decide which it is. This difficulty induced Werner to investigate similar compounds which contained no nitrogen and therefore could not form ammonium salts. The results of his investigations (Berichte 34, 3300; Liebig's Annalen 322, 296) are perhaps among the most important that have ever been obtained from work on oxonium salts. He started with



in which a carbonyl group

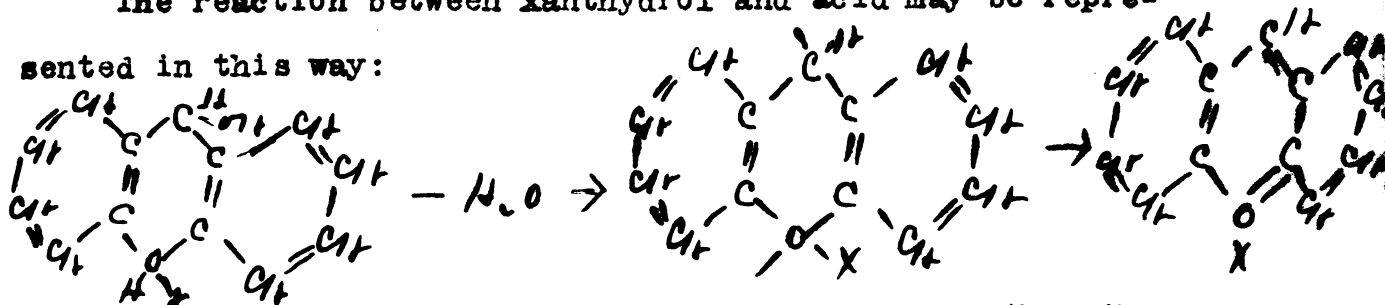
takes the place of the imid group in phenoxazine. On reduction xanthon gives xanthidrol, which, while it shows no pronounced basic properties, can nevertheless combine with acids, forming true salts. The hydrol



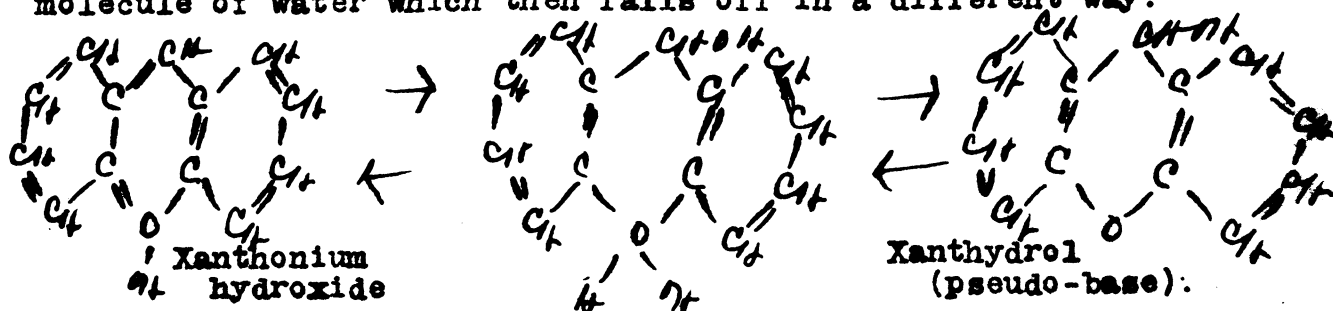
solves in concentrated acids, giving intensely colored solutions from which salts could not be isolated on account of their solubility. However, a difficultly soluble chlorplatinate and double salts of the chloride with ferric and mercuric chlorides were obtained and analysed. The analysis proves that xanthidrol forms monoacid salts with the loss of a molecule of water. Werner believed that an oxonium salt is formed which,

losing a molecule of water, goes into an orthoquinoid derivative in precisely the same manner in which the carbinols of the rosaniline bases lose a molecule of water to give salts which are generally considered to be paraquinoid derivatives.

The reaction between xanthidrol and acid may be represented in this way:



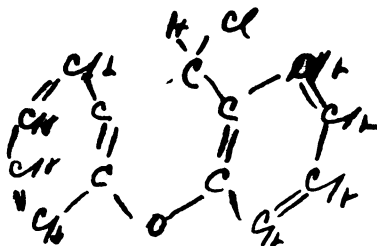
These salts Kehrman called carboxonium salts. In them the  $\text{CH}^+$  group replaces the nitrogen atom of azoxonium salts. The salts correspond to a base which is presumably unstable, going over into the more stable, isomeric xanthidrol by absorbing a molecule of water which then falls off in a different way:



These reactions are quite analogous to those of rosaniline bases when they are freed from salts by alkalies. They go over into isomeric carbinols, which are colorless.

With the loss of water and salt formation in acid solutions there is the formation of an orthoquinone group. As is usual with this rearrangement the salts formed are intensely colored while the original substance is colorless. This circumstance is a great support to Werner's theory for the formation and constitution of these salts. There is only one other possible structure for these salts, that of an alkyl chloride of

a secondary alcohol

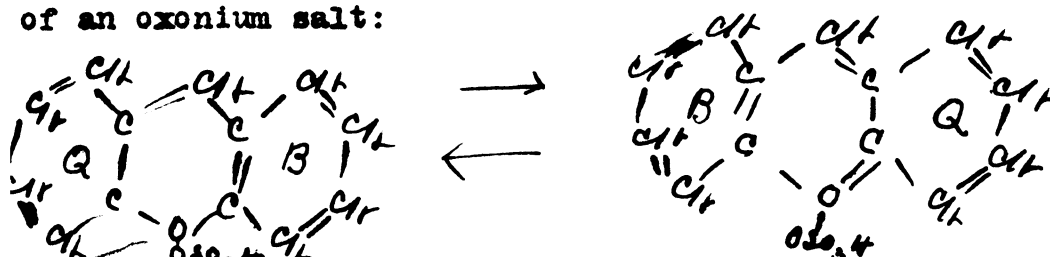


But there is

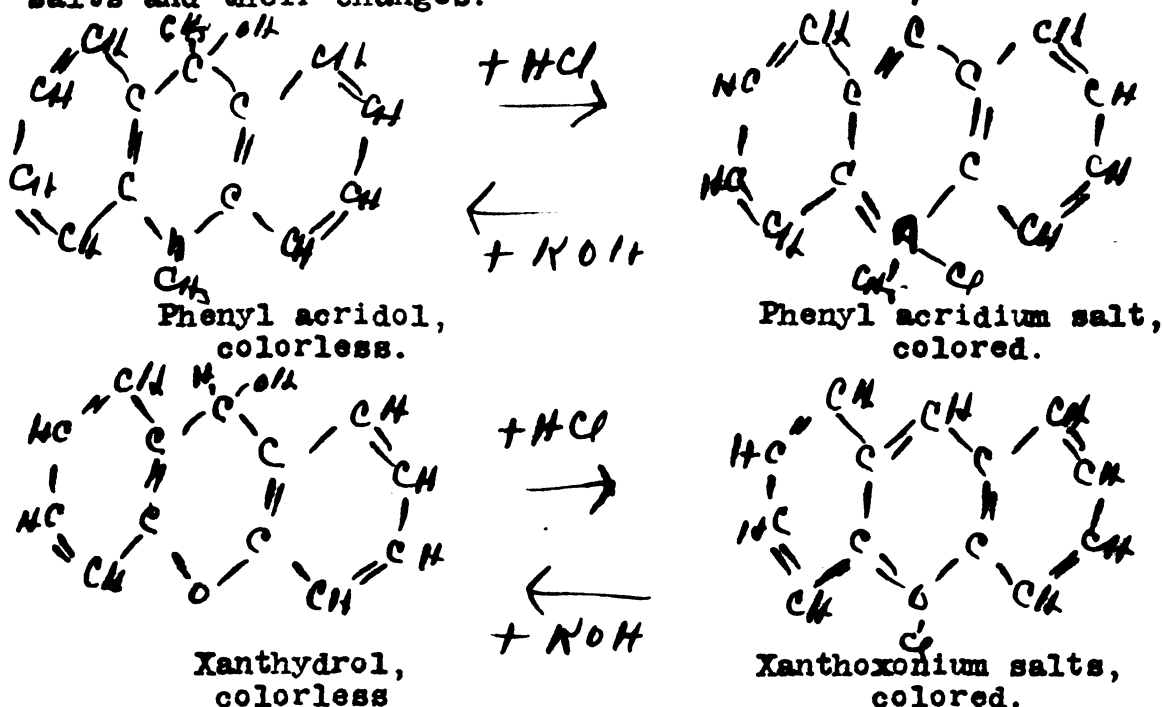
no reason why such a compound should have either a saltlike character or color. At present the burden of evidence is in favor of Werner's theory. In Part V Baeyer's latest ideas are given on the nature of rosaniline and analogous dyes. He decides that they are carbonium and not ammonium salts and that their color is due to the contrast between the positive and negative parts of the molecule (Rosenstiehl's structure), instead of any quinoid structure. In Part V it is intended to show that the older views concerning the quinoid structure are probably to be accepted and that the very reasons which caused Baeyer to reject this theory really confirm it. These salts prepared by Werner, therefore, probably represent the type of fully alkylated oxonium salts  $R = O \begin{matrix} R' \\ \diagup \\ X \end{matrix}$ . Both Werner and Kehrman have prepared corresponding salts of sulphur compounds, the azthionium and carbthionium salts, which have properties confirming the conclusions reached in regard to the oxygen derivatives.

Carboxonium salts similar to those prepared by Werner were also studied by Hewitt (Berichte 34, 3819 (1901) ), in his investigations on the theory of fluorescence of organic compounds. Before he prepared the salts he predicted (Zeitschrift für Physikalische Chemie 34, p.1) that such salts could exist, and moreover that they would be fluorescent, as there were two tautomeric forms and that oscillation between the two possible forms would produce fluorescence. To the sulphate of xanthydrol, in concentrated sulphuric acid, he ascribed the structure

of an oxonium salt:

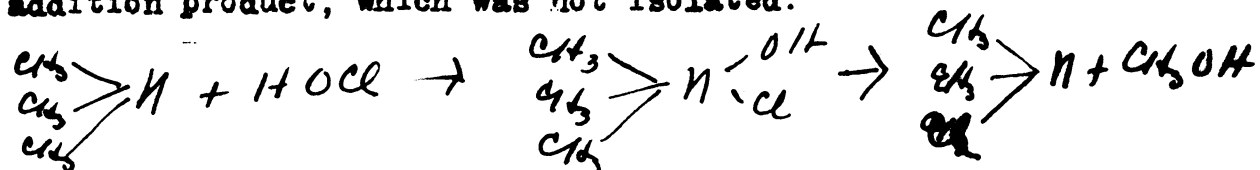


The constant shifting of the quinone and benzene groups in such a salt would produce constant oscillation between two tautomeric forms and this in turn would produce fluorescence. He makes a comparison between carboxonium salts and acridinium salts and their changes.



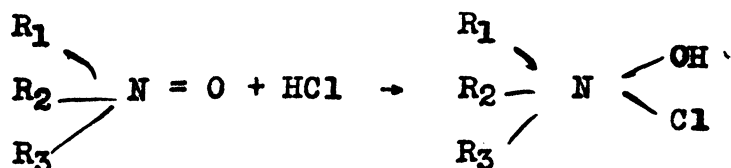
The salts of the trialkylamin oxides,  $R_3N - O \begin{matrix} H \\ \diagup \\ Cl \end{matrix}$  must also be considered as oxonium salts, in which the oxygen atom is combined with no carbon atoms. Willstaetter (Berichte 33, 1631) found that chlorimides of secondary amines are formed very easily by the action of hypochlorous acid on tertiary amines, a molecule of alcohol being split off. He thought the reaction could be explained by the formation of an unstable intermediate

addition product, which was not isolated.

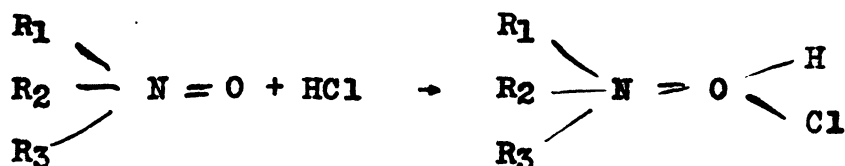


These unstable addition products have the same composition as the hydrochlorides of corresponding trialkyl amine oxides.

These hydrochlorides Wolffenstein, Bamberger and Hatzsch and others have found to be remarkably stable. These chemists have given them the constitution which would result from adding hydrochloric acid to the double bond between nitrogen and oxygen, thus:



But Willstaellen on the basis of the instability of the addition products of tertiary amines and hypochlorous acid, and in view of Collie and Tickle's work, suggests that salt formation is due to the oxygen atom giving oxonium salts.



### III. PHYSICO-CHEMICAL BEHAVIOR OF OXONIUM BASES AND SALTS.

The methods of physical chemistry have been applied to the investigation of oxonium salts principally in two directions. First, they deal with the proof that the compounds are not so-called "molecular compounds," but true salts, i.e., electrolytes. Secondly, they deal with the question of the quadrivalence of oxygen, as this is assumed in the constitution given

to oxonium salts.

Collie and Tickle by their investigation of the compounds of dimethyl pyrone started the modern development of the question of oxonium bases. They give results of conductivity experiments made by Kellas (Journal of the Chemical Society 75, 717). He used dimethyl pyrone and hydrochloric acid. The measurements showed that in more concentrated solutions dimethyl pyrone is partly but only partially combined with the acid, indicating a condition of partial dissociation and partial combination, such as exists in solutions of salts of very weak bases with strong acids.

But the salt-like character has been established more certainly by the quantitative equilibrium experiments with salt solutions made by P. Walden and by J. Walker, who worked independently but published their results about the same time. Coehn also contributed valuable results which proved that acid solutions of dimethyl pyrone give a positive ion which under the influence of the electric current moves to the negative pole. Sacken by experimenting with other oxonium compounds, principally the salts of cineol, confirmed the results obtained by Coehn.

Walden (Berichte 34, 4185) worked along five different lines. First he made a qualitative colorimetric determination for hydroxyl ions in aqueous solutions of dimethyl pyrone, with violuric acid. This test gave a negative result, showing that dimethyl pyrone can at best be only a very weak oxonium base. The rest were quantitative physical chemical experiments. He tried the effect of dimethyl pyrone solutions on the speed of birotation of grape sugar--which is a very delicate test for hydroxyl ions; the effect of dimethyl pyrone on the physical



equilibrium of water and benzene solutions of picric acid; the effect of dimethyl pyrone on the lowering of the freezing point of water produced by hydrochloric acid; the effect of the electric current on solutions of salts of dimethyl pyrone. In the first experiment he used the fact that hydroxyl ions increase the speed of birotation of grape sugar, even as weak a base as aniline doing so in a marked manner. But the addition of dimethyl pyrone solution to one of grape sugar caused no appreciable change in the velocity constant obtained for grape sugar in water solution. ( $K = .0243$  for water and  $.0237$  for a dimethyl pyrone solution.) Hence Walden concluded that dimethyl pyrone, if a base at all, can be only an exceedingly weak one.

In the next experiment he tried to prove that a salt is formed by dimethyl pyrone and picric acid by determining the change in the ratio between the concentration of picric acid in water solution and the concentration of picric acid in benzene solution when in a state of equilibrium, caused by the addition of dimethyl pyrone to the water solution. To do away with errors introduced by the ionization of picric acid he determined the ratio for each solution of picric acid separately and then the change in the proportion resulting from the addition of the pyrone to the same solution. For instance, he found:

$$\frac{C_{\text{benzene}}}{C_{\text{water}}} = 2.01, \quad \frac{C'_{\text{benzene}}}{C'(\text{water} + \text{pyrone})} = 1.94$$

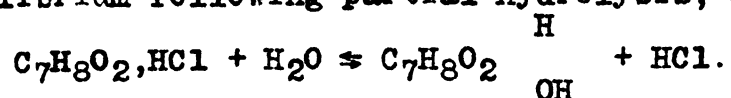
where  $C$  = concentration or gram molecules of picric acid per liter. Evidently some picric acid has combined with some pyrone. But as the ratio would be changed whether the picric

acid was taken up by dimethyl pyrone as a true salt, i.e., an electrolyte or merely as a molecular combination, no new proof was added to the oxonium base theory. And Collie had already proved that dimethyl pyrone and picric acid give a well crystallized compound of some sort.

The quantitative determination of the ionisation constant of dimethyl pyrone was the result of Walden's third experiment. The constant was only three times as large as the dissociation constant for water ( $H\ OH = 1.2 \times 10^{-14}$ ) showing that dimethyl pyrone is nearly as weak a base as water. Freezing point determinations of solutions of varying concentrations of hydrochloric acid in water and of the same solutions with the addition of dimethyl pyrone show that the depression produced by a given weight of dimethyl pyrone when added to the acid is not as much as when added to water alone. This is accounted for by the disappearance of a certain number of molecules, some of the pyrone having combined either with hydrogen ions to give new pyronium ions--two molecules giving one--or with hydrogen chloride to give an addition product which does not ionize. Walden considered only the first possibility. This conclusion has, however, been in a measure confirmed by conductivity measurements and by the proof given by Walker that hydrogen ions disappear from the solution of hydrochloric acid by the addition of dimethyl pyrone, the catalysis of methyl acetate, which is a function of their concentration, being slower.

Walden calculated the concentration of the positive pyronium ions in a given solution from the observed differences in the depression of the freezing point and knowing the amounts

of acid and pyrone used he could by difference calculate the concentrations of uncombined pyrone and uncombined acid. For a given solution he could calculate the concentrations of free base, free acid and positive ions or salt formed. These figures then enabled him to determine the ionisation constant according to the Arrhenius-Walker method as follows: A solution of a salt of a weak base and a strong acid is in a condition of equilibrium following partial hydrolysis, as



As for any base we have

$$(1) C_{\text{positive ions}} \times C_{\text{OH ions}} = k_{\text{base}} \times C_{\text{molecular base}}$$

$C = \text{concentration of gram molecules per litre}$

For dilute solutions we also have

$$(2) C_H \times C_{OH} = k_{\text{water}} = 1.2 \times 10^{-14} \quad (\text{Van 't Hoff, Physical Chemistry, Vol.I, p.131.})$$

From (1) and (2)

$$(3) \frac{C_{\text{positive ions}}}{C_H \times C_{\text{molecular base}}} = \frac{k_{\text{base}}}{k_w} = K_{\text{hydrolysis}}$$

But in dilute solutions salts and strong acids are completely and proportionately ionized, so we are allowed to substitute  $C_{\text{salt}}$  and  $C_{\text{acid}}$  for  $C_{\text{positive ions}}$  and  $C_H$  ions; and at the same time the base is practically all molecular, we may put  $C_{\text{base}}$  for  $C_{\text{molecular base}}$ . Then

$$(4) \frac{C_{\text{salt}}}{C_{\text{acid}} \text{ and } C_{\text{base}}} = \frac{k_{\text{base}}}{k_{\text{water}}} = K_{\text{hydrolysis}}.$$

(3) and (4) are respectively Arrhenius' and Walker's equations for the hydrolysis of salts of weak bases and strong acids.

For dimethyl pyrone hydrochloride we have

$$\frac{C_{\text{pyronium ions}}}{C_{\text{acid}} \times C_{\text{pyrone}}} = \frac{k_{\text{base}}}{k_w} = K_{\text{hydrolysis}}.$$

Walden by using values found for the pyronium ions, the free acid, and the free pyrone by cryoscopic measurements obtained as a constant

$$K_{\text{hydrolysis}} = 2.5 \text{ (mean of } 1.5 - 2.7 = 2.9)$$

This makes the ionisation constant of dimethyl pyrone

$$k_{\text{base}} = 2.5 \times k_w = 2.5 \times 1.2 \times 10^{-14} = 3 \times 10^{-14}$$

This shows that next to water it is one of the weakest bases which have yet been examined. In comparison we have:

$$K_{\text{water}} = 2.2 \times 10^{-16} \quad (\text{Affinity constant and not the constant of dissociation.})$$

$$K_{\text{urea}} = 1.5 \times 10^{-14}$$

$$K_{\text{pyrone}} = 3 \times 10^{-14}$$

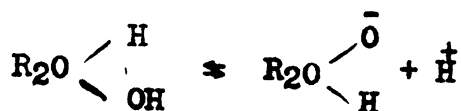
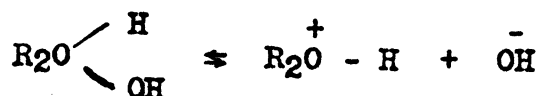
$$K_{\text{aniline}} = 5.3 \times 10^{-10}$$

$$K_{\text{ammonia}} = 2.3 \times 10^{-5}$$

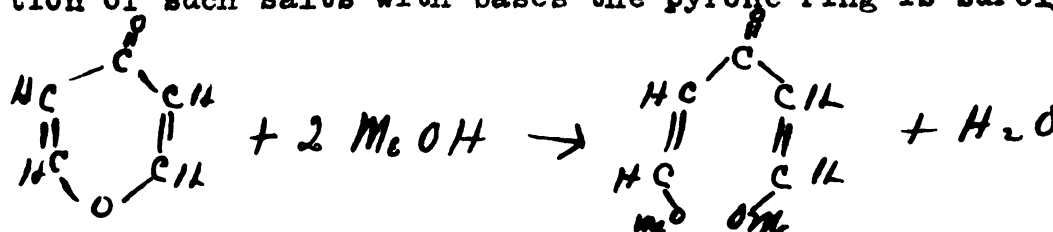
Walden obtained, by conductivity measurements, a constant which agrees well with this finding for dimethyl pyrone.

$$K_{\text{hydrolysis}} = 2.0 \text{ (mean of } 1.7 - 2.2 - 1.9 - 2.0)$$

Walden showed by similar methods that dimethyl pyrone possessed acid as well as basic properties, i.e., it is amphoteric. His conclusion was that quadrivalent oxygen must have acid as well as base forming properties and that a hydroxide  $\text{R}_2\text{O} \begin{smallmatrix} \text{H} \\ \diagup \\ \text{OH} \end{smallmatrix}$  must ionize in two ways.



Undoubtedly dimethyl pyrone has acid properties, as recent work of Collie and Tickle (Journal of Chemical Society 85, 971) and Willstaetter (Berichte 38, 1461) has confirmed. But Willstaetter's conclusions from his results is that in the formation of such salts with bases the pyrone ring is surely opened,



and the salts are salts of bivalent rather than quadrivalent oxygen.

At the same time that Walden made his estimate of the ionization constant of dimethyl pyrone Walker <sup>(*Ann.* 34, 41N (1901))</sup> made determinations of the degree of hydrolysis of the hydrochlorides of di- and tetra methylpyrone, using catalysis methods. In this way he ascertained the amount of free acid in the hydrochloride solution by its catalytic action on methyl acetate. He used as a comparison equivalent solutions of urea hydrochloride. For all three bases he found practically the same amount of free acid in both  $\frac{n}{10}$  and  $4\frac{n}{10}$  solutions. Previously he had proved the degree of dissociation for urea hydrochloride is about 90 per cent. in  $\frac{n}{10}$  and 70 per cent. in  $4\frac{n}{10}$  solutions, and so he decided upon the same figures for the pyrones. He did not calculate the constant of hydrolysis, but by using the ionization constant of urea we obtain  $k_{\text{base}} = 1.5 \times 10^{-14}$ , which agrees very well with Walden's results. Sacken (Berichte 35, p.1212), reversing Walden's experiment, proving that dimethyl pyrone increases the solubility of picric acid in water as compared to that in benzene, showed that cineol, the base with which he

experimented, is more soluble in acid solutions than in pure water and also more soluble in strong acids as hydrochloric and nitric than in as weak an acid as acetic. On the other hand, it is more soluble in pure water than in alkaline solutions. The combination of these results leads to the conclusion that cineol behaves toward acids as a base.

The physico-chemical evidence so far presented has not proved directly that oxonium salts are electrolytes, but their ionization has been shown directly. Coehn (Berichte 35, p. 2673) by electrolysing a solution of the hydrochloride of dimethyl pyrone, proved that dimethyl pyrone migrates toward the negative pole and therefore must form a positive ion. Walden showed that dimethyl pyrone in pure water or in liquid sulphur dioxide conducts the electric current, although poorly. Sacken used cineol as a solvent for hydrogen chloride and found that the molecular conductivity of the latter decreases on dilution with cineol, as the conducting acid decreases in proportion as the formation of the cineol salt increases. To make this conclusive he tried the same experiments with solutions of hydrogen chloride in aniline and in toluidine, obtaining the same results. While this result is to be expected with a solution of an acid in a basic solvent, it does not prove that a true salt is formed, as the conductivity would decrease no matter what sort of a compound is formed with hydrogen chloride.

These results at least demonstrate the existence of oxonium salts in solutions as electrolytes and establish the fact that dimethyl pyrone is an exceedingly weak base of the order

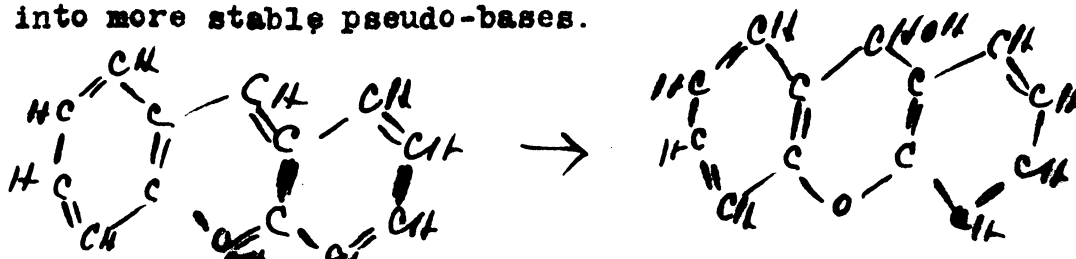
of water and urea. We can then realize what exceedingly weak bases the oxonium bases must be as dimethyl pyrone is one which<sup>6</sup> forms oxonium salts particularly readily, a fact to which their discovery by Collie and Tickle is due. Whether oxygen as a basic element has very weak ionizing powers or whether the

real bases  $R_2O \begin{smallmatrix} \nearrow H \\ \searrow OH \end{smallmatrix}$  are unstable and lose a molecule of water,

thus breaking down into non-ionisable molecules,

$R_2O \begin{smallmatrix} \nearrow OH \\ \searrow H \end{smallmatrix} \rightleftharpoons R_2O + H_2O$ , and leaving only an exceedingly small amount of ionizing hydroxides present at any given moment, cannot yet be definitely decided. It may well be the instability of the oxonium hydroxides rather than the weak ionising power of the oxonium bases to which the very small constants are due. In the case of alkylated ammonias there is a sudden marked increase in basic strength in going from trialkylated amines to quaternary ammonium hydroxides. The change is coincident with and probably due to the sudden increase in stability of the hydroxides  $R_4NOH$  as compared with  $R_3N OH$ . So far fully alkylated oxonium salts have not been prepared, the carboxonium and azoxonium salts  $R = \underset{\underset{R}{|}}{O} - X$  being the nearest ap-

proach to them. The bases also are very unstable, going over into more stable pseudo-bases.



so that the study of the hydrolysis of these salts will not remove the difficulties met with in the case of pyrone salts.

Physical Chemistry and Quadrivalence of Oxygen.

Perhaps the earliest idea of the quadrivalence of oxygen was presented by *Ure* in 1864 (Comptes Rendus 58, 381). He drew an analogy between oxygen and sulphur, selenium, and tellurium, which can also be quadrivalent. That oxygen might be quadrivalent in hydrogen and barium peroxide was advanced by Buff in 1866 (Theoretische Chemie 63, 77). In 1869 Williamson (Journal of Chemical Society 22, 360) considered the possibility of oxygen being quadrivalent in carbon monoxide and in the same year Jorgensen thought that oxygen in water might be quadrivalent making a bivalent radicle  $(OH_2) <$  as the radicle  $(NH_3) <$  is in some compounds. J. Thomsen in 1873 (Berichte 6 6, 433) gave oxygen four valences in order to explain the constitution of diperic acid. In 1875 Friedel (Bulletin de la Societe Chimique 24, 160) ascribed four valences to oxygen in the compound of ethyl ether and hydrochloric acid, from which the chemistry of oxonium bases and salts really developed. Tilden a year later (Introduction to Chemical Philosophy, 1876) attempted to explain water of crystallization, in zinc sulphate, for instance, by making oxygen quadrivalent. Wurtz also used this same explanation. In 1884 Jorgensen (Journal für praktische Chemie 29, 419) again suggested that Water  $(H_2O) <$  might be a bivalent radicle just as  $(NH_3) <$  Bamberger in 1891 (Berichte 24, 1761) gave four valences to the oxygen atom in five atomic rings, such as furfurane, oxazole furzane. In 1893 Kurnakow (Journal der russischen chemischen Gesellschaft 25, 726) took for granted a quadrivalent oxygen atom in all hydrate compounds.



Upon the basis of spectrum analyses *Kaunonikoff*  
 (Journal der russischen chemischen Gesellschaft 32, 639) assumes the quadrivalence of oxygen in numerous carbon compounds containing oxygen as well as in some compounds containing nitrogen. It is interesting to note that Baeyer and Villiger formed oxonium salts from the very same compounds. Important work along this same line was done by Brühl in 1895 (Berichte 28, 2847; 30, 163; 33, 1710; Zeitschrift für physikalische Chemie 18, 514) and his results are a valuable contribution by physical chemistry to the question of quadrivalent oxygen. He made very careful spectrometric measurements with pure hydrogen peroxide and found that it has a much higher molecular refraction and dispersion than a molecule,  $\text{H.O.OH}$ , should have calculated from the data obtained for water and for hydrogen. The molecular refractions  $M_\alpha$  of water and of hydrogen, for the  $\alpha$  line of hydrogen spectrum, and  $M_{\text{Na}}$  for the sodium line, and the difference between the refractions for the  $\alpha$  and  $\gamma$  hydrogen lines,  $M_\gamma - M_\alpha$ , are respectively

	$M_\alpha$	$M_{\text{Na}}$	$M_\gamma - M_\alpha$
HOH	3.69	3.71	.09
H	1.10	1.05	.04

By subtracting the values of hydrogen from those of water and multiplying the difference OH by two, Brühl found for  $\text{HOOH}$

	$M_\alpha$	$M_{\text{Na}}$	$M_\gamma - M_\alpha$
Calculated	5.18	5.32	0.10
Found	5.79	5.82	0.14

A higher valence of oxygen is suggested by the large differences between the calculated and the experimental values. As

he considered the refractive power a most valuable criterion he gave to hydrogen peroxide the formula  $H - \overset{\overset{|}{\text{O}}}{\text{O}} - H$ , since no compounds are known in which oxygen or any other element of the sulphur group shows any tendency toward trivalence. Brühl also concluded that water itself has two free valences,  $H - \overset{\overset{|}{\text{O}}}{\text{O}} - H$ , and that its great role as an ionizing solution may be due to these free valences. Ostwald had suggested this same possibility when the theory of ionization was first advanced. In a recent important paper Walker supports this same view. Since hydrogen peroxide is more unsaturated than water Brühl predicted that it would have a higher dissociating power and this conclusion has since been indirectly confirmed by the determination of the dielectric constants of hydrogen peroxide, which is 92.8 against 81 for water.

#### IV. THE CONSTITUTION OF OXONIUM SALTS.

In 1876 Friedel assigned to the hydrochloride of methyl

H

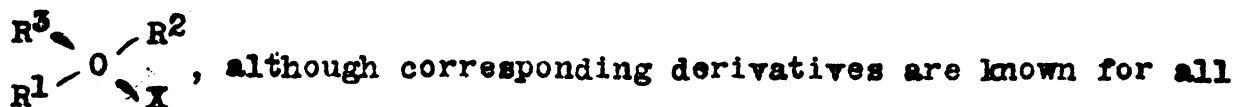
ether the constitution  $CH_3 - O - CH_3$  and this has been gen-

Cl

erally accepted as the type of all oxonium salts. Such a constitution assumes a quadrivalent oxygen atom bound to three alkyls or hydrogen atoms and an acid radicle. The evidence for such a constitution at present is the following:

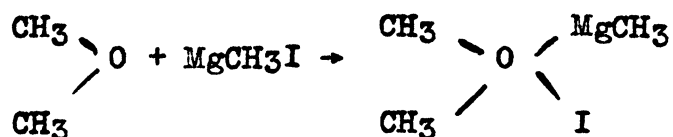
(1) In the formation of such oxonium salts oxygen takes its place among other elements which form a long and well-known series of strictly analogous salts in a precisely similar manner. The best known of these are the ammonium salts ob-

tained from ammonia and amines, in which the nitrogen atom changes from trivalent to quinquivalent  $R^1R^2R^3N + R^4X \rightarrow R^1R^2R^3R^4NX$ . In the same series we have the phosphonium,  $R_4PX$ , arsonium,  $R_4AsX$ , and stibonium salts,  $R_4SbX$ , and a corresponding series of the long-known bases and salts derived from the sulphur group of elements. In this case also the element changes its valences, as it is found in its hydrogen compounds, in forming bases and salts when one positive and one negative radicle are taken up. Thus are formed sulphonium salts  $R_3SX$ , selenium salts  $R_3SeX$ , and tellurium salts  $R_3TeX$ . Oxygen, as the first member of the sulphur group is represented in this series by oxonium salts. Iodonium salts were discovered in 1894 by V. Meyer. Iodine, which is univalent in its hydride, changes to trivalent in its salts, such as  $(C_6H_5)_2IX$ . In Part V will be mentioned salts which are probably chloronium salts, although Baeyer, who has recently discovered them, does not seem to have recognized them as chloronium salts. The other series of salts, however, from ammonium to iodonium salts, are well established and from their analogy to these salts it seems justifiable to assume the constitution ascribed to oxonium salts. As yet we know no oxonium salts in which the oxygen holds three alkyls

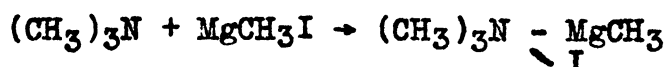


the other salts of this kind, often being the only well-defined salts of the series. Baeyer explained the absence of such fully alkylated salts by considering extremely weak bases, like methyl ether, unable to compose alkyl halides like methyl iodide (Berichte 35, 1201). He thought he might obtain an analogous

derivative by experimenting with Grignard's magnesium methyl iodide and methyl ether and he succeeded in doing this. The reaction he represented thus:



Tscheligen (Berichte 37, 2081) has recently found that magnesium alkyl iodides combine in a similar manner with trimethyl amine:



Carboxonium and azoxonium salts also represent a special type of fully alkylated compounds  $\text{R} = \text{O} \begin{array}{c} \text{R} \\ \diagup \\ \text{X} \end{array}$ .

(2) In the salt obtained by Friedel we must either accept the quadrivalence of oxygen, for which we have evidence, or a higher valency than one for hydrogen, or a higher valency than four for carbon, for neither of which is there the slightest indication worthy of consideration in any department of chemistry. The most important evidence for the quadrivalence of oxygen may be summed up as follows: the spectrometric measurements of Brühl and Kannonikoff (discussed in Part III); the position of oxygen in the periodic system; the similarity between oxygen and sulphur compounds; the striking analogy between water and ammonia. These facts, in absence of contradicting evidence, lead us to accept the constitution adopted by Friedel for the hydrochloride of methyl ether and to regard it as a type of many other similar salts, according to the ideas of structure laid down by Kekulé. Werner, however, has developed an entirely different theory for the structure of

oxonium bases (Berichte 34, 3300; Liebig's Annalen 322, 296).

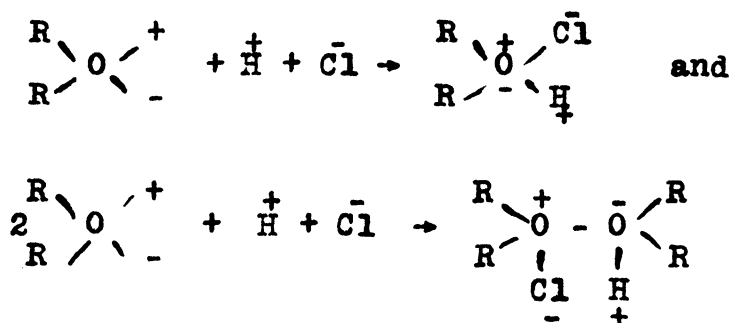
As his views concerning valence and structure are not generally accepted, no further reference to them will be given; but they are fully explained in the papers mentioned.

The structure of three other classes of oxonium salts requires special consideration. First the salts of oxonium bases which have unsaturated carbon bonds in the molecule; second, salts which have more than one molecule,  $R_2O$ , combined with one molecule of acid,  $HX$ ; third, those which have more than one molecule of acid combined with one molecule of alkyl oxide. The salts of the first of these classes will be discussed in Part V, as they have been subjected to thorough and important investigation by Baeyer.

Salts of the second class are described by Wallach, who prepared a cineol hydrochloride,  $(C_{10}H_{18}O)_2HCl$ , and by Archibald and McIntosh (Journal of the Chemical Society 85, 919), who recently prepared and analyzed a number of similar salts of acetone and ether with halogen acids. They have given this

constitution: 
$$\begin{array}{c} R \quad R \\ \diagdown \quad \diagup \\ O - O \\ \diagup \quad \diagdown \\ R \quad R \\ | \quad | \\ H \quad Cl \end{array}$$
 This is particularly inter-

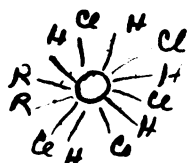
esting from the point of view of the electrical theory of valence:



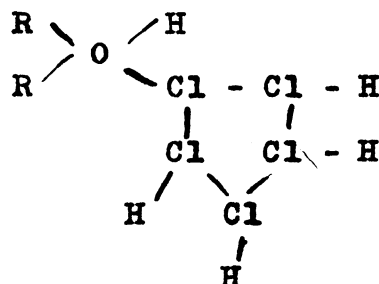
Probably much the same combinations occur in the case of metal

ammonium compounds, such as  $\text{AgCl}, 2\text{NH}_3$ .

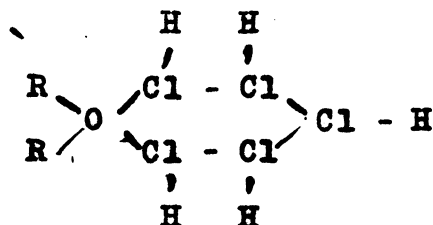
Salts  $\text{R}_2\text{O}, x\text{HCl}$  have also been studied by Archibald and McIntosh. They treated several organic oxygen derivatives, such as ethers and acetone, with anhydrous liquid halogen acids at very low temperatures, having previously found that these gave good conducting solutions, and obtained well-defined, crystalline salts. Some of the most interesting of these are the diacetone monoiodide and compounds such as diacetone pentahydrochloride  $\left[(\text{CH}_3)_2\text{CO}\right]_2, 5\text{HCl}$ , and methyl ether pentahydrochloride  $(\text{CH}_3)_2\text{O}, 5\text{HCl}$ . They consider oxygen in the latter compound to have twelve bonds, and give the following structure:



That the halogen is polyvalent is far more probable. The structure might then be represented according to the ideas of Remsen concerning the double chlorides and salts of complex chloro acids. We <sup>might</sup> have, therefore,



making the halogen atoms trivalent, as Remsen assumed them to be. Archibald and MacIntosh themselves mention a possible structure

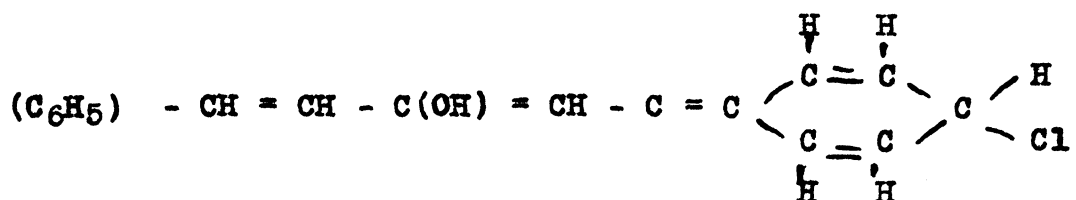


But as no oxonium salts have yet been prepared of the composition  $R_2O \begin{smallmatrix} \diagup X \\ \diagdown X \end{smallmatrix}$ , in which oxygen appears as a diacid base, the former structure is to be preferred.

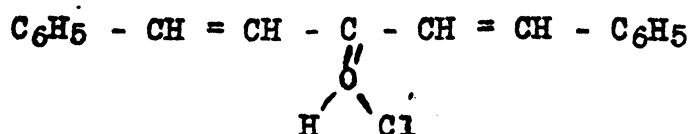
## V. APPLICATIONS TO CHEMICAL THEORY.

### OXONIUM VERSUS CARBONIUM BASES.

In his remarkable first paper on oxonium bases Baeyer referred to the possibility of carbon under certain conditions acquiring basic properties, and to the difficulty which might arise of distinguishing whether we have a carbonium or an oxonium salt in a given case. In a late paper (Berichte 35, 1189) he emphasizes this difficulty and calls attention to the colored complex salts of triphenyl methyl chloride with stannic chloride and similar chlorides, and to the red hydrochloride of dibenzal acetone. Kehrman had already suggested for the latter a quinoid structure



rather than the structure of an oxonium salt



The question of carbonium versus oxonium salts arises particularly when the molecule is decidedly unsaturated.

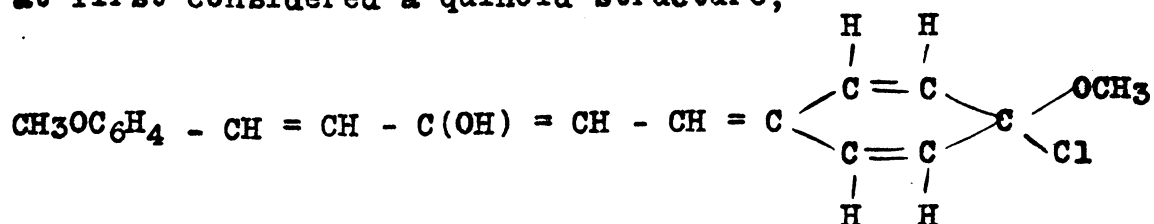
This same question had appeared in the chemistry of nitrogen derivatives in distinguishing between ammonium salts and



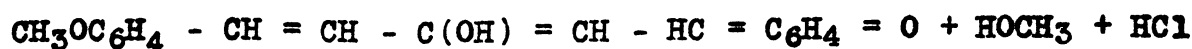


investigations, he has changed his decision three or four times. At one time he favors the carbonium theory, at another the quinoid ammonium (also oxonium) theory. An experimental and historical development of the facts will be briefly summarized and the conclusion most consistent with these facts presented.

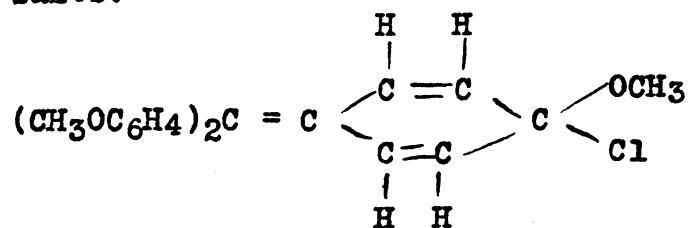
In order to test the quinoid structure of the salts of dibenzal acetone, Baeyer prepared the corresponding salts of dianisalacetone which gave just as intensely colored salts. He at first considered a quinoid structure,



impossible, since the salts do not lose alcohol to form a quinone:



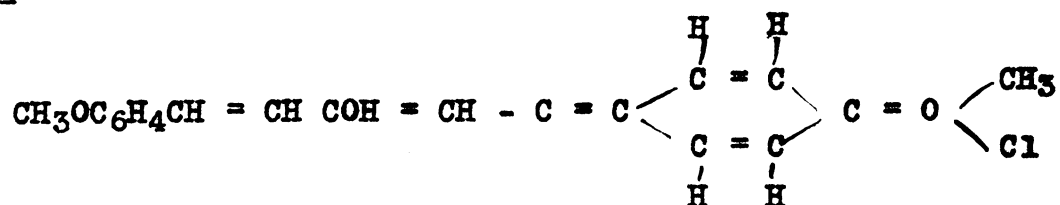
Next he prepared trimethy triphenyl carbinol and found that it too formed intensely colored salts which are stable and do not lose alcohol. He thought that they could not be quinoid salts:



and they must therefore be carbonium salts  $(\text{CH}_3\text{OC}_6\text{H}_4)_3\text{C}^+ - \text{Cl}^-$ , corresponding to the constitution which Rosenstiehl gave to rosaniline.

Later experiments with rosanilines forced him to accept for a time a quinoid structure for dianisalacetone and the salts of trimethoxy triphenyl carbinol, making them real

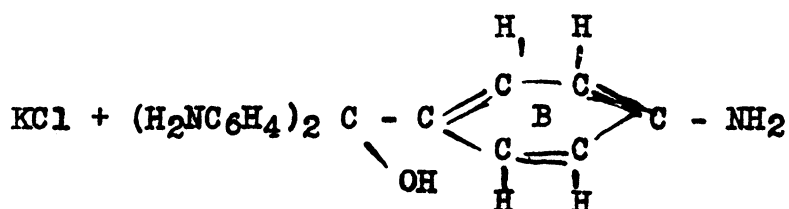
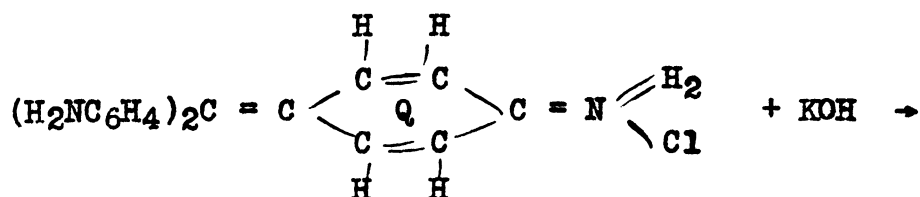
oxonium salts.



Such salts would not lose alcohol readily, judging from the stability of ethers towards aqueous acids.

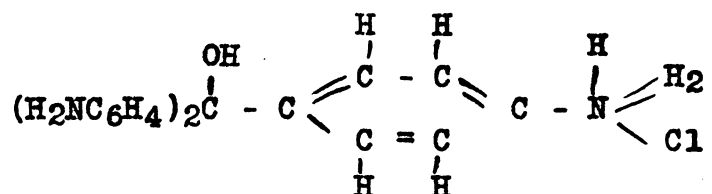
In his latest paper, however, he has reverted to his first opinion concerning their structure, for reasons considered below.

Finding that he could come to no definite conclusions from these experiments, Baeyer next investigated the analogous amido derivatives of triphenyl methane and with these he made important discoveries. Ordinarily when a colored salt like rosaniline hydrochloride (magenta) is treated with an alkali, liberating the base, the color disappears and the resulting colorless compound holds a molecule of water instead of the molecule of acid in the colored compound--unlike any other primary amines known. The quinoid theory of these dyes represents the reaction thus:

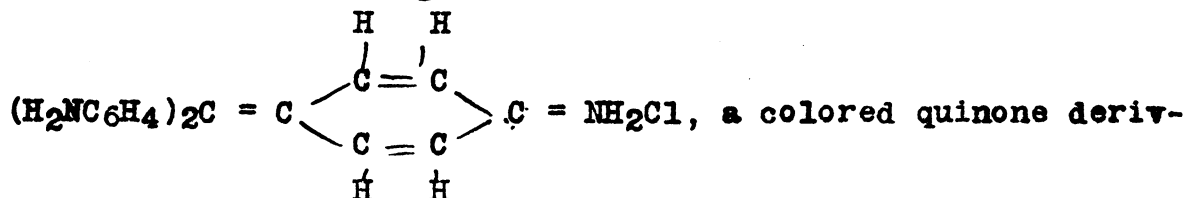


This colorless substance is triamido triphenyl carbinol, which has a benzene nucleus, B, instead of a quinoid nucleus, Q. By

addition of acid the color returns, not instantly but fairly rapidly, the salt being formed thus:

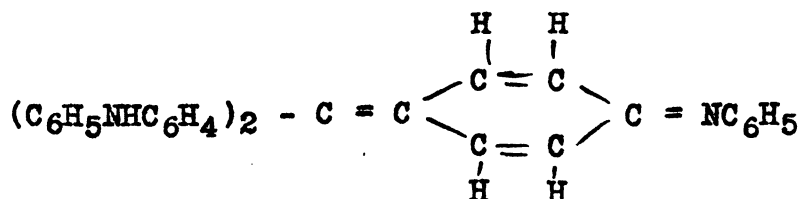


and this ~~imine~~ <sup>aniline</sup> water gives



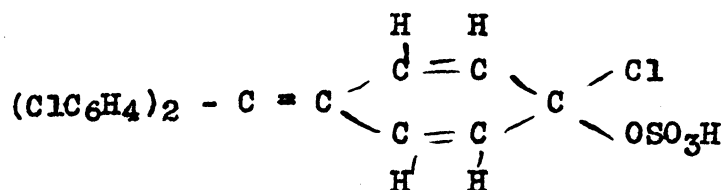
ative.

The explanation according to the carbonium theory is that the colored salt  $(\text{H}_2\text{NC}_6\text{H}_4)_2\text{C}^+ - \text{Cl}^-$  owes its color to the contrast between the acid radicle and the basic amine radicles. Then the free base is the carbinol  $(\text{H}_2\text{NC}_6\text{H}_4)_3 - \text{COH}$ , and this is colorless because the contrast between positive and negative groups is not so great. By using almost anhydrous alkalis to liberate the bases, Baeyer prepared from certain of the rosaniline dyes, especially "aniline blue," anhydrous bases which were most deeply colored, instead of colorless carbinols. The anhydrous base obtained from aniline blue can have but one constitution. It must be a quinone derivative.

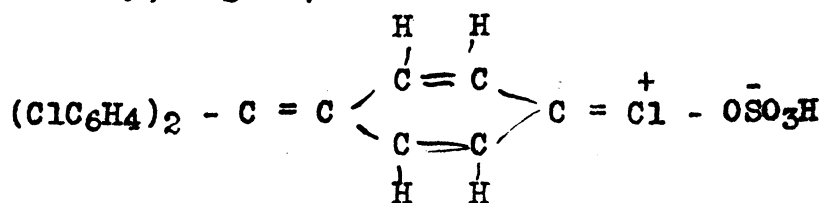


It is black and must owe its intense color to the quinone nucleus. The discovery of these fundamentally important anhy-

drous bases caused Baeyer to reject the carbonium formulae for the colored nitrogen and oxygen derivatives of triphenyl carbinol and again to accept the quinoid constitution. But in his latest paper (Berichte 38, 569) he considers the quinoid structure out of the question and develops a theory for color and carbonium salts by modifying Rosenstiehl's view by modern electro-chemical ideas. The experimental work on which he bases his latest views were carried out with ppp-trichlotriphenyl carbinol and ppp-tr<sup>4</sup>iodotriphenyl carbinol. These were treated with concentrated sulphuric acid and gave intensely colored salts, which gave no trace of silver halide in twenty-four hours when treated with silver acetate in glacial acetic acid. Therefore he said they could not be quinoid derivatives:

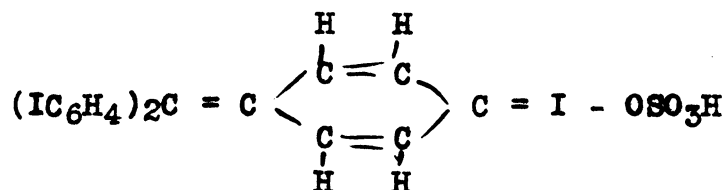


It is probable that he has again fallen into the error he made in the case of salts of dianisol acetone and trianisyl carbinol, when he concluded that they would lose alcohol readily and afterward that as oxonium salts they would be stable. In all probability he has made the noteworthy discovery of the first well-defined chloronium salts (see Journal of American Chemical Society, August, 1905):



and of an iodonium salt of the same sort as was investigated

by V. Meyer:



Naturally such salts would give no silver halide, just as potassium chlorate or iodate do not.

Some important phases of the question have not yet been investigated, but the weight of evidence at the present time favors the quinoid theory of color and this in turn favors the ammonium and oxonium salt formation instead of isomeric carbonium salt formation. Therefore we consider salts such as those of dianisolacetone and trianisyl carbinol true oxonium salts.

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I wish to take this opportunity to express my sincere thanks to Dr. Stieglitz for his kind assistance.