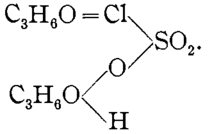
The analyses of the acetone compound gave:

Preparation I: 47.3, 47.0;
" II: 48.4, 49.0.

A compound consisting of two molecules of acetone and one of acid has 50.1 per cent. acid, so that the product is $(C_3H_6O)_2,HClSO_3$, and its constitution is:



MACDONALD CHEMISTRY BUILDING,
MCGILL UNIVERSITY, MONTREAL,
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[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

ON CHLORONIUM SALTS.

BY JULIUS STIEGLITZ AND EDITH E. BARNARD.

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BAEYER'S epoch-making investigations[1] on the question of the constitution and the source of color of the triphenylmethane dyes, which grew out of his great work on oxonium salts, have been followed with especial interest by the one of us, because the results promised to throw light on three fundamental questions, in which he has been interested. In 1899[2] attention was called to the necessity of a careful investigation of the question whether the salts of certain carbimide derivatives, such as the imido-esters, are ammonium salts, $R_2C : (\underset{+}{N}RHX)$, or true salts (not esters or ester salts) of carbon ions $R_2\overset{+}{C}(NH_2)$. All the experimental evidence favoring the latter view, the existence of carbon ions, $R_3\overset{+}{C}$, was suggested and adopted, their formation was supposed to be greatly favored by the presence of imide groups but not limited to imide derivatives[3]. The question, however, is an exceedingly delicate one and physico-chemical measurements carried out since with imido-esters[4] have again raised doubts as to the correctness of the conclusion reached, and we are now inclined rather to the view that the salts are really ammonium salts and

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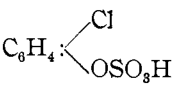
[1] *Ber.*, **35**, 1189, 3013 (1902); 36, 2774 (1903); **37**, 597, 2818, 3191 (1904); 38, 569 (1905).

[2] *Am. Chem. J.*, **21**, 101 (1899).

[3] *Loc. cit.*, p. 111.

[4] The results will be published shortly.

that the evidence favoring the existence of carbonium salts may be due to the possibility of tautomeric derivatives, $R_2CCl(NH_2)$ and $R_2C : NH_2Cl$. Since then, the idea of carbon ions, carbon bases and carbon salts has been much more developed and greatly advanced, especially by the work of Gomberg, Kehrmann and Baeyer. The same problem of ammonium (and oxonium) salts *versus* carbonium salts confronted Baeyer and Villiger in the great investigations mentioned above, for instance the problem whether the rosaniline dyes are quinoid ammonium salts $(NH_2C_6H_4)_2C : C_6H_4 : NH_2Cl$ (1), or carbonium salts, $(NH_2C_6H_4)_3C.Cl$ (2), in which the three amide groups simply intensify the positive character of the carbon atom. And, indissolubly connected with this problem is the question whether these dyes owe their color, as hitherto supposed, to the quinoid group in (1) or to the contrast between the positive and the negative groups in (2)—a question in which the theory of indicators[1] is most vitally concerned. The difficulty of reaching a decision in this case as in that of the imido-esters is shown by the fact that the experimental results favored first one view, then the other, but the very fact that Baeyer had the great fact of color to aid him led us to believe that his experimental material would more readily lead to a final decision of the problem than would the colorless carbimide salts under investigation here.

In his latest paper, Baeyer[2] describes most intensely colored salts of trichlor- and triiodotriphenyl carbinol, and the existence of these colored salts has led him to reject the quinoid-ammonium form (1), as representing the constitution of the intensely colored salts of triphenylmethane dyes and to accept and develop that of the colored carbonium salts (2). The salts of the above halogen derivatives do not give a trace of silver halide with silver acetate in glacial acetic-sulphuric acid solutions, even in the course of twenty-four hours. For this reason the quinoid constitution, $(ClC_6H_4)_2C$:  $C_6H_4 : \left<\begin{matrix} Cl \\ OSO_3H \end{matrix}\right.$, is rejected and the carbonium constitution, $(ClC_6H_4)_3C.OSO_3H$, accepted. There is, however, another quinoid structure for these intensely colored salts of the halogen derivatives of triphenylcarbinol, a structure which not only restores our confidence in the quinoid theory of color but also suggests to us

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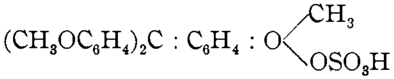
[1] Stieglitz: This Journal, **25**, 1112 (1903).

[2] *Ber.*, **38**, 569 (1905).

that Baeyer has most likely made the beautiful discovery of the first well-defined representatives of the long expected class of *chloronium* salts. The structures we would propose are $(ClC_6H_4)_2C : C_6H_4 : Cl.OSO_3H$ and $(IC_6H_4)C : C_6H_4 : I.OSO_3H$ for the chloronium and the iodonium salts, as corresponding to the oxonium salts,



$(CH_3OC_6H_4)_2C : C_6H_4 : O\begin{smallmatrix} \diagup CH_3 \\ \diagdown OSO_3H \end{smallmatrix}$, and to the ammonium salts, $(NH_2C_6H_4)_2C : C_6H_4 : NH_2Cl$.

Basic properties of chlorine have long been anticipated and have been suggested by W. A. Noyes[1], Stieglitz[2], Walden[3] and others. Positive chlorine in such a combination would not readily give silver chloride with silver acetate. Iodonium salts, $R_2I.X$, corresponding to the above assumption, have, of course, long been known, having been obtained, in particular, from phenyl iodides, just as the above salts are derivatives of phenyl halides. The structures suggested are, therefore, not only rational but such compounds have been anticipated with the very properties that Baeyer's beautiful discovery shows them to possess.

In further support of our views we would bring briefly:

(1) The fact discovered by Baeyer that the free imide bases are undeniably quinoids and intensely colored, $(NH_2C_6H_4)_2C:C_6H_4:NR$.

(2) The production of color, as Baeyer repeatedly points out, is intimately connected with the presence of benzene nuclei in a molecule, as is also the power to form quinoid nuclei.

(3) According to the carbonium theory, we must have two different carbinols $(RC_6H_4)_3C.OH$, $(R = CH_3O; H_2N; Cl; I)$, of exactly the same composition and structure, one a true alcohol, that does not ionize to any extent, the other a pronounced base, forming a well-defined salt, which, in the case of a rosaniline, reacts neutral. Such a change of properties without a change of structure or valence ought to be assumed only when all ordinary alternatives fail.

(4) This is likewise true for the acceptance of the same constitution for colorless salts, $(C_6H_5)_3C.Cl$, and intensely colored salts, $(C_6H_5)_3C.Cl, SnCl_4$. The color of the latter salts, described by Norris and Sanders, Kehrmann, Gomberg and others, has been

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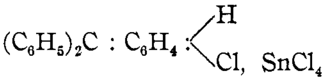
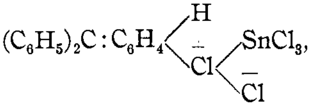
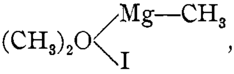
[1] This Journal, **23**, 460 (1901).

[2] *Ibid.*, **23**, 796 (1901).

[3] *Z. physik. Ch.*, **43**, 385 (903).

explained by Kehrmann as being due to their being salts of an isomeric quinoid chloride,  $(C_6H_5)_2C : C_6H_4 : \left< \begin{array}{l} H \\ Cl,\ SnCl_4 \end{array} \right.$; that is, Kehrmann considers them to be carbonium salts of a bivalent carbon base, $(C_6H_5)_2C = C_6H_4 <$. It is probable, however, that they are really quinoid chloronium salts,  $(C_6H_5)_2C : C_6H_4 \left< \begin{array}{l} H \\ \overset{+}{Cl} \left< \begin{array}{l} SnCl_3, \\ \overset{-}{Cl} \end{array} \right. \end{array} \right.$ corresponding to the oxonium salts,  $(CH_3)_2O \left< \begin{array}{l} Mg—CH_3 \\ I \end{array} \right.$, prepared by Baeyer,[1] and to an ammonium or metal ammonium, salt RNH_3Cl. In other words the basic, not the acid, properties of chlorine account for their formation.

(5) Triphenylmethyl chloride is a conductor, especially in acid solvents (sulphur dioxide),[2] and the conducting solutions are colored; the conductivity in acid solvents is as valid an indication of triphenylmethyl chloride being a base—a chloronium base in its quinoid form—as of its being a salt of a carbonium base, as has been argued heretofore. Dimethylpyrone shows exactly the same behavior, forming conducting solutions of oxonium salts in acid solvents.

We do not consider the evidence we have presented as being by any means conclusive but we do believe that our views agree rather better with the facts than does the carbonium theory and that (1) the existence of the long sought chloronium bases will be dated from Baeyer's work and that the endeavor to obtain simpler chloronium salts ought to be undertaken with renewed hope; (2) the quinoid theory of the triphenylmethane dyes should still be maintained; and (3) the existence of true carbonium salts, both in the case of the carbimides and of the triphenylmethane derivatives, is still open to grave doubts.

CHICAGO, June 6, 1905.

NOTE.

The Crystallization of Sodium Iodide from Alcohols.—An accidental observation during the preparation of some ethers by Williamson's method led to the experiments detailed below, which are

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[1] *Ber.*, **35**, 1201 (1902).

[2] Gomberg: *Ibid.*, **35**, 2397 (1902); Walden: *Loc. cit.*