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A THEORY OF HALOCHROMISM

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The phenomenon of halochromism, particularly in the triaryl carbinol series, has been the subject of numerous researches. The discussions on the nature of the rearrangements taking place when a colourless carbinol is transformed into a coloured, salt-like substance have been reviewed so often, in textbooks as well as in the current literature, that I have thought it unnecessary to specify the majority of the earlier contributions here.

The purpose of the present paper is to outline a theory of halochromism which covers a considerable number of different types of halochromism. Some of the details have, of course, been expressed by others before, explicitly or implicitly, clearly or vaguely, but as far as I can see, the present theory avoids the contradictions and difficulties inherent in the earlier theories.

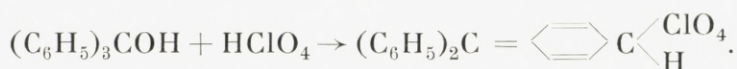
1. The triaryl carbinols.

It seems to be generally admitted that the change of colour occurring when a triaryl carbinol is dissolved in e. g. conc. sulphuric acid is intimately connected with the transformation of a non-polar substance — the carbinol — into an ionised salt:



All solutions of the coloured compounds of this type display electrical conductivity and colourless solutions do not. Often esters of the carbinols can be isolated as colourless compounds which in some solvents — as ether and benzene — form colourless solutions, and in other solvents — e. g. liquid sulphur dioxide — are coloured. These esters thus show tautomerism between a non-ionised and an ionised form, the equilibrium depending upon the solvent. Very recently this tautomerism has been the subject of an interesting paper by K. ZIEGLER (*Ann.* **479**, 90 (1930)) who has determined the equilibrium for different triarylmethyl chlorides in liquid sulphur dioxide by means of conductivity measurements.

It is evident that the change of colour must be due to some change in the structure of the triarylmethyl complex, but on this point no general agreement has been reached at the present time. GOMBERG explains the generation of colour by assuming a quinone structure of one of the benzene rings and assuming the corresponding p-carbon atom to be bound to the anion:



(This view was originally advanced by KEHRMANN, but has been advocated more by GOMBERG than by KEHRMANN himself). The theory has developed from the quinonoid formulation of the triphenylmethane dyes. Although most European chemists deny the possibility of a quinone formulation it must be admitted that GOMBERG and coworkers have found reactions which strikingly show that some inner rearrangement must have taken place in the benzene rings when the carbinol or its esters are transformed into

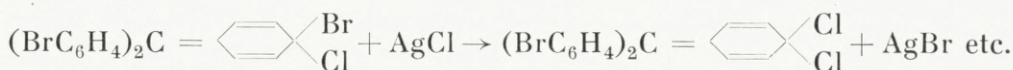
coloured salts. Thus, when p-bromo-triphenylmethyl chloride is dissolved in liquid sulphur dioxide it will on standing be partly transformed into the isomer compound p-chloro-triphenylmethyl bromide. GOMBERG explains this fact by assuming an equilibrium:



If tri-p-bromotriphenylmethyl chloride dissolved in liquid sulphur dioxide is shaken for some time with silver chloride the following reaction takes place:



In this reaction GOMBERG assumes that all three benzene rings become successively quinonoid and are then able to react with silver chloride:



It must, therefore, be admitted that the formulation usually applied for the triarylmethyl ion simply as a complex ion R_3C does not account in any way for the peculiar chemical reactivity of p-halogen in the benzene rings. On the other hand, the quinone theory offers no satisfactory explanation of the physico-chemical properties of the salts. The ionisation of the salts involves the assumption that this p-carbon atom becomes the bearer of the positive charge. The stability of the salts is not in favour of this assumption; but still more difficult to understand is the influence of substituents in all three benzene rings upon the "basic" properties of the triarylmethyl complex. This influence is decidedly symmetrical. Even when the assump-

tion is made that the quinoidation in a symmetrically substituted compound is permanently shifting from one ring to another, it is difficult to explain how, at a certain instant, the substitution in the two benzenoid rings is able to exert any considerable influence upon the para carbon atom in the quinone ring in regard to its tendency to become ionised. Furthermore, while ortho and para substituents greatly influence this tendency, the meta substituents only slightly do so in spite of the fact that they are in ortho position to the para carbon atom, and for this reason might be expected to influence the properties of this carbon more than in any other position.

This influence of substituents may be very marked even if these are rather neutral, see e. g. the polymethoxylated triphenyl carbinols, *J. Am. chem. Soc.* 1927, **49**, 1354.

The formulations of methoxy-substituted triphenyl carbinol salts as oxonium compounds (KEHRMANN, Houben-Weyl, *Methoden der organischen Chemie*, Leipzig 1923, vol. III, p. 345) may undoubtedly be considered a failure, and the close relationship which evidently exists between p-methoxy and p-dimethylamino-substituted triphenylmethyl salts strongly indicates a similarity in structure of these intensely coloured compounds. From the bivalency of oxygen in the methoxy compounds one must deduce free amine character in the triphenylmethane dyes of the crystal violet and fuchsine type. The classic formulation of these dyes as quinoid ammonium salts must, in my opinion, be abandoned.

The author, in his doctor's dissertation (*Studier i Triphenylmetangrupper*, Copenhagen 1926) has made an attempt to explain the different halochromic phenomena upon the assumption that it is the methane carbon atom which

splits off an electron, when a salt is formed, and becomes positively charged. Hereby a high potential arises in the centre of the complex, and this potential will cause displacements in the electron orbits of the benzene rings. These perturbations will in some instances loosen, in others fasten the electrons to their respective nuclei, depending upon the positions in the molecule. As a consequence the energy required to remove the electrons from their normal into higher quanted orbits will be in some cases greater, and in others smaller, than before. In other words, the light absorbed will be partly of higher and partly of lower frequency in the salts than in the carbinols or esters. That is exactly what happens. Certain substituents produce very high absorption bands, and when these bands are found within the limits of the visible spectrum the compounds are intensely coloured. It is now very conspicuous that p-substituents of this type (oxygen and amino groups) produce very high narrow bands, while ortho substitution gives broader and lower bands. This phenomenon, too, is explained by the theory, since any electrical effect from the centre of the molecule will be much more symmetrical in the para position than in any other. In this influence of the electric charge upon the para-position the cause of the altered chemical properties of the p-halogen substitutes must also be sought. It is impossible at the present time to go into details as to the mechanism of this influence. The aromatic ring structure seems in some way or other to be a conductor of electricity.

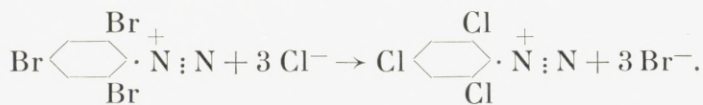
Another effect of the central charge is displayed in the polymethoxy triphenylmethyl salts which in acid aqueous solutions have a marked tendency to be hydrolysed in the para methoxy groups yielding the corresponding phenols

and methyl alcohol. The charge converts the anisol into an ester of a strong acid $R_2C^+ \langle \text{benzene ring} \rangle OH$, and the ester is therefore hydrolysed readily in acid aqueous solution. It must be expected that the chemical properties of ortho and meta substituted compounds are somewhat altered although it has not as yet been possible to find any purely chemical consequences analogous to those mentioned in the case of para substitution.

The author's views regarding the halochromism may be briefly summarised as follows: The necessary and sufficient condition for the development of halochromic colour is that the methane carbon atom becomes electrically charged, the surrounding benzene rings thereby being exposed to a one-sided electrical influence which alters the electron orbits, and thereby also, more or less, the nature of the bonds between benzene carbon and substituents.

The same applies to the diphenylmethane series and probably also to toluene derivatives although cations of this type are unknown. Anions of the type $C_6H_5CH_2^-$, however, are coloured; such ions are present in solutions of benzyl-alkali metals.

Attention is called to a very interesting analogy between the effect of a charged carbon atom and a charged nitrogen atom attached to a benzene ring: When tribromoaniline is diazotised in a concentrated alcoholic solution of hydrogen chloride, the bromine in the benzene ring is slowly, but fairly quantitatively replaced by chlorine:



(Hantzsch, Ber. **30**, 2351 (1897).)

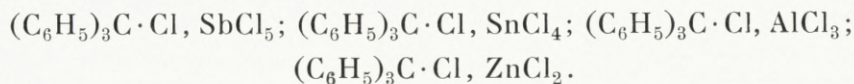
The analogy with the GOMBERG reaction is striking.

In some ways the theory outlined above may be considered a revivification of Baeyer's "wave-line" valence, but the present knowledge of atomic structure and the fairly clear differentiation between homoeopolar and heteropolar valences allow of a more definite conception of the processes involved in the transitions from one state to the other.

By drawing an analogy between carbon and nitrogen the concept of carbon as the bearer of the charge in the R_3C kations acquires a deeper significance. In ammonium salts, whether substituted or not, the nitrogen is tervalent as in ammonia: in the NH_4 -ion the same number of valence electrons are present as in NH_3 . In the R_3C ions the carbon may analogously be considered bivalent; the halochromism consists in a transformation of quadrivalent into bivalent carbon. In harmony with this concept of the process is also the fact that in several cases the transformation takes an observable and sometimes measurable time, e. g. in the reaction between crystal violet and sodium hydroxide and the reaction between heptamethoxy triphenyl carbinol and carbonic acid.

2. Complex compounds of triarylmethyl chloride.

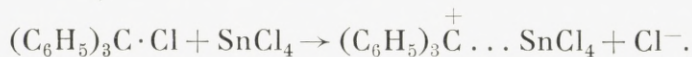
A series of addition compounds of triarylmethyl chloride and metalloids or metal chlorides is known. The following types have been prepared:



The series is completed when compounds of the type $(C_6H_5)_3C \cdot Cl, HCl$ are added.

All these compounds are coloured and their solutions

conduct the electricity. The colours of the solutions are very nearly identical with the colour of the corresponding "simple" salts (perchlorates). It is therefore to be assumed that the same rearrangement of the triphenylmethyl complex has taken place. But while it is easily understood that acids, i. e. hydrogen ions, are able to remove the hydroxyl groups from the carbinols, it may seem somewhat peculiar that the said halogenides should be able to remove the chlorine as chloride ions from the triarylmethyl chlorides. Besides, not only chlorine but also other acid anions are removed from colourless triarylmethyl esters quite analogously to the removal of chlorine. The explanation is probably to be sought in the fact that carbon has the coordination number 4 and has a marked tendency to fill out its coordination number. When, therefore, e. g. stannic chloride is added to a solution of triphenyl methyl chloride, the stannic chloride molecule attaches itself to the carbon, which, however, is unable to hold five groups and consequently splits off the chlorine as a chloride anion:



The reaction, if this explanation is correct, is quite analogous to e. g. the following:



and a whole series of analogous reactions known from the complex metal compounds.

This theory in a very simple way explains the colour of these salts, since the ions contain the ionised triarylmethyl group. The individual influences of the different halides explain the slight variations in colour displayed by

the different complex salts. It places in a natural way the "acid salts" in this group. These are only stable in solutions in which hydrogen chloride is not dissociated, and the same is true for all the other complex salts. That the hydrogen chloride is present in a non-ionised state is evident from the fact that the HCl molecule can be removed by passing a stream of dry air either over the solid compound or through a solution or suspension of it in a suitable solvent. This procedure is often of use in the preparation of the "normal" chlorides.

When colourless triarylmethyl esters are dissolved with colour in liquid sulphur dioxide it is probably due to the formation of complex cations $R_3C^+ \dots SO_2$.

The peculiar phenomenon which can be observed when hydrogen chloride is passed into a solution of triphenyl carbinol in ether, viz. that the solution at the first moment turns yellow but after a short time becomes colourless, may be explained by the formation of an unstable hydrated ion $(C_6H_5)_3COH + HCl \rightarrow (C_6H_5)_3C^+ \dots H_2O + Cl^-$. In coloured aqueous solutions of triarylmethyl salts the cations are probably hydrated.

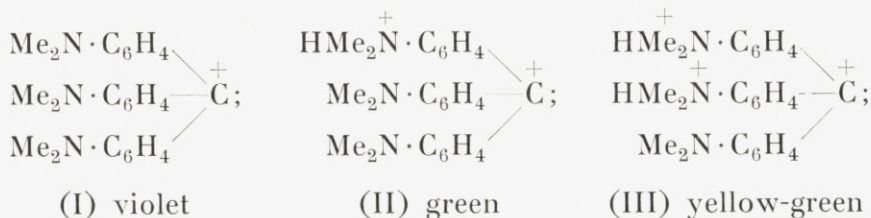
Another interesting fact should be mentioned in this connection. When triphenylmethyl is prepared from triphenylmethyl chloride and zinc, only two thirds of the chloride is transformed into the free radical. One third forms the complex salt $(C_6H_5)_3C \cdot Cl, ZnCl_2$ and this is not reduced by the metal. The reason is that zinc cannot remove the charge from the triphenylmethyl ion in the benzene solution; the triphenyl methyl is a more electropositive "metal" than zinc under these conditions.

3. The influence of electrical charges upon the colour.

The reason for the change of colour of acid and base indicators is to be sought in a change of the electric charge of the indicator molecules or ions. The colour of an aminoazo compound is different from that of the corresponding ammonium ion. The colour of an undissociated acid may be different from that of the corresponding ion. The rearrangements in such molecules or ions are probably closely related to the rearrangements outlined in the triarylmethane group. The theory thus brings a very great number of phenomena under the same point of view. A further extension of its applicability will be outlined later in this paper.

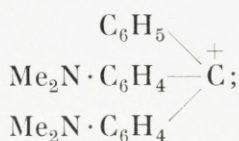
A simple but very beautiful illustration of the effect of electrical charges upon the colour is found in the effect of hydrogen ions upon crystal violet. This substance dissolves in pure water with a deep violet colour. When a little hydrochloric acid is added the solution turns green and at a certain p_H the solution has a striking resemblance to one of malachite green. When more acid is added to either of these solutions the colour changes gradually and in nearly the same way through yellow-green into an orange-yellow colour. On dilution the shades return in the opposite succession.

The different colours are due to the following ions formed

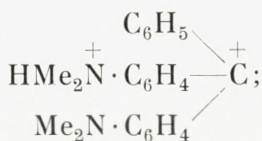




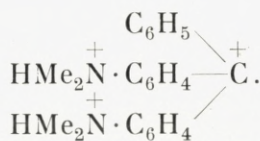
(IV) orange



(V) green



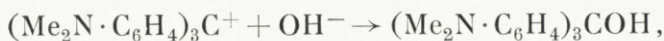
(VI) yellow-green



(VII) orange

It is seen that when an amino group is transformed into an ammonium group, its influence upon the colour is very slight, in accordance with the fact that now the charges are nearly equal at both ends of the benzene ring in question. However, the four charges in ion (IV) do have some effect upon the absorption of the benzene ring; while the colour of triphenyl carbinol in conc. sulphuric acid is only a comparatively weak yellow, the ion (IV) is intensely coloured; the absorption band has moved further into the visible region and is much higher than in the case of the unsubstituted triphenylmethyl ion.

In order to complete the scheme above it may be mentioned that when sodium hydroxide is added to solutions of (I) or (V) the colour gradually disappears due to the reaction



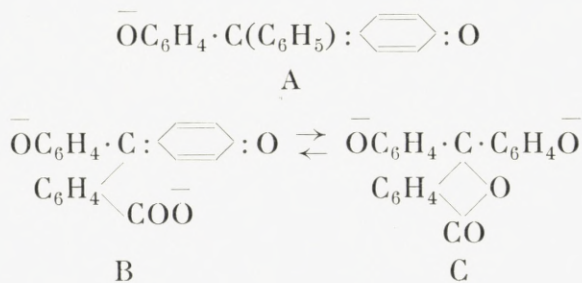
and analogously for V.

When the ionisation disappears the colour disappears. Inversely, the colour reappears gradually when an equivalent amount of hydrochloric acid is added.

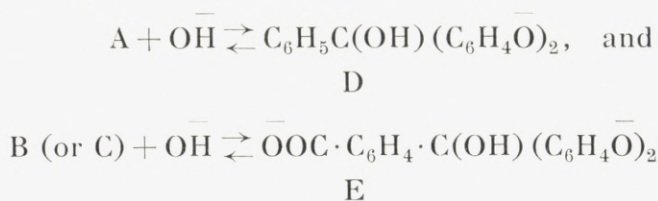
4. Benzaurine, phenolphthalein, and related compounds.

When benzaurine or phenolphthalein are dissolved in sodium hydroxide the solutions are coloured intensely red-violet. In the solid state phenolphthalein is colourless, while benzaurine is red, approximately as minium. When the usual preparation of benzaurine is analysed the carbon and hydrogen content corresponds to that of a mixture of p-dihydroxy-diphenyl carbinol and an anhydride of this compound. After some time's heating to 90° , water is removed and the analysis corresponds to the pure anhydride. This substance is usually given the formula $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_5) : \text{C}_6\text{H}_4 : \text{O}$, i. e. a derivative of diphenyl methylene quinone.

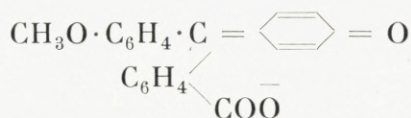
In the red solutions benzaurine forms a univalent, phenolphthalein a bivalent anion. They are attributed the formulae A and B, resp.



The ion B is supposed to form a lactoid ion (colourless) C, and a tautomeric equilibrium is assumed between B and C. Both solutions will in excess of hydroxide gradually fade, due to the reactions

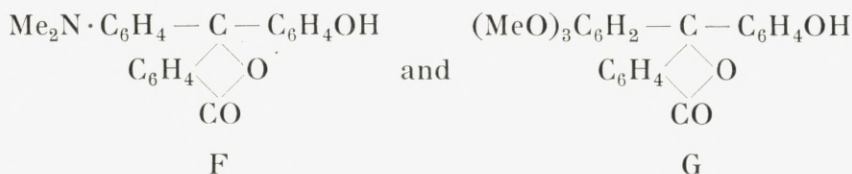


The resp. bivalent and tervalent ions D and E are colourless. The fading processes are reversible and are pronounced time reactions, whereas the formation of A or B from the original substances seems to be instantaneous. The quinonoid structures listed above originate from FRIEDLÄNDER (Ber. **26**, 172 (1893)) who transferred the quinone formulation of the amino compounds to the oxygen derivatives. This formulation is, however, far from satisfactory. Phenolphthalein monomethyl ether is only slightly coloured (yellow) in alkaline solution although a quinonoid form is supposed to be formed:



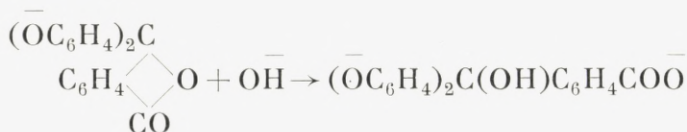
The formation of a quinone ring is obviously not sufficient cause for the strong colour displayed by the ions A and B. In order to surmount this difficulty a modified quinone theory has been advanced by ACREE (Am. Chem. J. **37**, 71 (1907)), the so-called quinone-phenolate theory assuming a certain interaction between a quinone group and a phenolate group within the same molecule. This theory is closely related to the oscillation theory of BAEYER (Ann. **354**, 163 (1907)). The quinone phenolate theory has recently been supported by A. THIEL (Sitzungsber. der Ges. zur Beförderung der Ges. Naturwiss. zu Marburg **62**, 472 (1927)) in an interesting paper on substituted phenolphthaleins, dealing particularly with their optical properties.

This modified theory, however, also has to face a number of difficulties. It fails to explain why compounds such as



are intensely coloured in alkaline solutions. They have indicator properties quite similar to phenolphthalein. The molecular extinction coefficients in the maxima of the absorption bands of these compounds are of the same order of magnitude as that of phenolphthalein, whereas that of phenolphthalein monomethyl ether is far smaller. ϵ_{max} is for phenolphthalein about 33000, for F and G about 16000, but for the monomethylether about 40. In order to explain this remarkable difference the theory has to be extended considerably.

Another fact seems strange: phenolphthalein and similar compounds in solution assume their full colour intensity instantaneously when sufficient alkali is added, but on standing the excess of hydroxyl ions slowly decolorise the coloured ions. In other words: according to the theory hydroxyl ions are able to 1) transform a benzene ring into a quinone ring and 2) afterwards transform the quinone ring slowly into a benzene ring. On the other hand, when the solution is neutralised the quinone ring is instantaneously transformed into a benzene ring. — The fading reaction has been interpreted as a reaction between the lactoid form of the phenolphthalein anion (C) and a hydroxyl ion, thus consisting in the opening of a lactone ring, a reaction which is known to be, in many cases, a slow reaction:

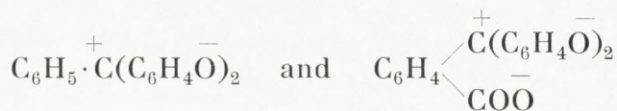


This explanation, however, cannot be correct. If the equilibrium $B \rightleftharpoons C$ does exist it must necessarily establish itself instantaneously because a phenolphthalein solution assumes its maximum colour intensity immediately after the addition of sodium hydroxide, and then the fading proceeds regularly.

As this dynamic equilibrium involves the opening of the lactone ring, the slowness of the fading reaction cannot be explained on the said basis. Furthermore, the fading reactions of phenolphthalein and benaurine are quite analogous and the velocities are of the same order of magnitude; the carboxyl group, therefore, seems to play no essential part in the reaction. When, finally, it is remembered that crystal violet fades in a quite similar way in alkaline solution it seems reasonable to assume that it really is the coloured anion (B) of phenolphthalein which is the one reactant in the fading reaction.

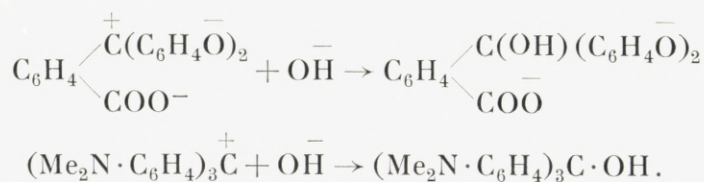
These remarks may suffice as a reason for some doubt as to the validity of the quinone formulations. In the following it will be shown that the formulation given here for the simple triaryl carbinol halochromism also applies to compounds of the phenolic derivatives.

When benaurine or phenolphthalein are dissolved in dilute sodium hydroxide the coloured ions formed are assumed to have the structures

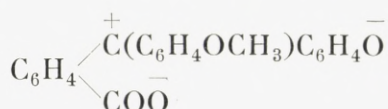


When formulated in this way the similarity between the different coloured triphenyl methane derivatives is evident. Common to all is the electrically charged methane

carbon. The fading of phenolphthalein becomes strictly analogous to the fading of crystal violet:



Phenolphthalein monomethyl ether forms the yellow anion



These and analogous formulae bring out clearly that substituents in all three rings exert an influence upon the colour of the ion. It explains that an amino group attached to a benzene ring containing no hydroxyl groups — as in dimethylanilin-phenol-phthalein — increases the visible absorption tremendously, just as it does in the case of the amino-triphenyl carbinols, e. g. when passing from dimethyl-amino-triphenyl carbinol salts to malachite green.

In the free state benzaurine has the formula $\text{C}_{19}\text{H}_{18}\text{O}_2$, and its constitution is, according to the theory presented here, to be written



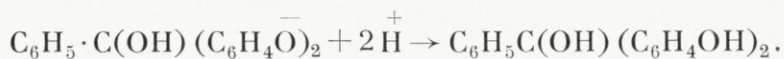
This compound may be considered the anion of an acid $\text{C}_6\text{H}_5 \cdot \text{C}^+(\text{C}_6\text{H}_4\text{OH})_2$. An ion of this composition must be assumed to be present in benzaurine perchlorate. It is a very strong acid; dissolved in water it is practically completely dissociated in benzaurine and H^+ . It may appear

strange that a phenolic compound of this type is a strong acid, but the phenomenon is not without analogies: When dibromo-*p*-aminophenol is diazotised a compound of similar nature is formed:



It seems that the positive charge on the nitrogen or carbon atom is able to repulse, through the benzene ring, the hydroxyl hydrogen in a way similar to what is known about the alifatic amino acids in which carboxyl anions and ammonium cations mutually induce increased strength as bases and acids. (The phenomenon is most striking in the case of the betains).

When an alkaline solution of benzaurine is acidified the precipitated benzaurine seems to be a mixture of the amphi-ion and the corresponding hydrate, *p*-hydroxy-triphenyl carbinol, which may be formed in the reaction between the faded ion and hydrogen ions:

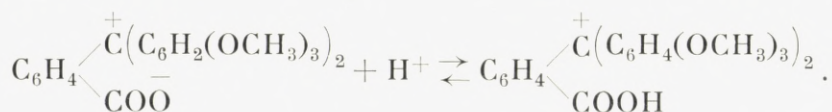


The precipitate is soluble in ether and benzene, but when the solutions are dried with calcium chloride most of the dissolved compound is precipitated. This behaviour is difficult to explain on the basis of the quinone theory because usually quinones are more soluble in the solvents mentioned than are the corresponding hydroxyl compounds.

Phenolphthalein itself may be a lactone, an inner ester of a dihydroxy triphenyl carbinol-*o*-carbonic acid. It is, however, a lactone with an extremely high velocity of the opening of the lactone ring. The first reaction between

phenolphthalein and hydroxyl ions takes an immeasurably short time. The opening of the lactone ring is not quite of the usual type, the hydroxyl group not being — or not instantly being — attached to the carbon atom, but it seems to be a phenomenon strictly analogous to the dissociation of a weak electrolyte.

If in the phenolphthalein molecule the phenol hydroxyl groups are replaced by dimethylamino groups, or the phenol groups with phloroglucinol-trimethyl ether, compounds are obtained which, also in the free state, appear to be ampho-ions. They are not attacked in any way by alkali, i. e. it is impossible to prepare alkali salts of the corresponding hydroxy-acids. Hydrochloric acid produces a violet solution of the methoxy compound, and at a certain p_H the amino compound forms a green solution; higher acidity, however, produces ammonium salts and the colour then disappears. With zinc chloride both compounds form intensely coloured compounds. The best explanation of these facts is, in my opinion, to consider the compounds as inner salts of a strong base with a somewhat weaker acid: Hydroxyl ions cannot unite with the carbon ion to form undissociated carbinol, whereas hydrogen ions are able to unite with the carboxyl ion forming an undissociated carboxyl group:



The fact that the two compounds are colourless in the solid state (and in neutral solution) may be due to the very short distance between the positive and the negative charge in these molecules; there will be no appreciable

electric forces acting upon the benzene rings and no visible colour is produced.

A direct proof of the existence of such amphi-ions might be obtained from measurements of dipole moments of the compounds in question. For experimental reasons, however, it seems to be a very difficult matter because these compounds all seem to be insoluble, or nearly so, in the solvents suitable for such measurements. In this fact, however, a fairly strong indication is found for the correctness of the views advanced here because typically polar compounds always are insoluble in benzene and similar non-polar solvents, and an aminosubstituted (usual) lactone might be expected to be fairly soluble in benzene.

The inadequacy of the quinone formulation might be proved if it could be shown that an optically active asymmetrical phthalein could be dissolved in alkali without losing its optical activity. To this end I have prepared some unsymmetrical phenolphthaleins, but have so far not succeeded in resolving them into active components due to the very poor crystallizing power of their salts with optically active bases. The experiments are being continued. According to a recent note by WALLIS¹ it has been possible to prepare an optically active derivative of a triaryl carbinol which after having been transformed into a complex, halochromic ferric chloride compound was recovered without racemisation. Details of the experiments have not been published yet, but supposing the statement to be correct it is highly probable that the same can be done in the phthalein or aurine series.

A chemical reaction which the amphi-ion theory explains in a simple way is the following: Fuchsone, the

¹ J. Am. Chem. Soc. 59, 812 (1931).

anhydride of p-hydroxy-triphenyl carbinol and usually ascribed the formula $(C_6H_5)_2C = \text{C}_6\text{H}_4 = O$, when treated with methyl magnesium iodide yields the compound $(C_6H_5)_2C(CH_3)C_6H_4OMgJ$. The quinone formulation would predict a quinol $(C_6H_5)_2C = \text{C}_6\text{H}_3 \begin{matrix} \diagup OMgJ \\ \diagdown CH_3 \end{matrix}$ whereas the ampho-ion interpretation is in agreement with the course of reaction actually followed.

The conversion of the quinonoid formulation into an "electrostatic" formulation of the change in structure occurring when a colourless hydroxyl compound is transformed into a coloured salt probably applies to several other forms of halochromism than those dealt with here. Besides in the rather closely related instances of halochromism displayed by diaryl ketones and ketones of the dibenzalacetone type it probably also applies to cases where the charged atom is not carbon but nitrogen or certain other atoms. Thus indophenols and indamines may be constituted as ampho-ions with a positively charged nitrogen atom, e. g. "Bindschedler's green": $((CH_3)_2N \cdot C_6H_4)_2N^+$ and quinone-mono-p-hydroxyanil, $HO \cdot C_6H_4 \cdot N : C_6H_4O$, in alkaline solution $(OC_6H_4)_2N^+$. Methylene blue may be attributed the formula $(CH_3)_2N \cdot C_6H_3 \begin{matrix} \diagup N^+ \\ \diagdown S \end{matrix} C_6H_3N(CH_3)_2$, etc. In these compounds the nitrogen must be regarded as electronically univalent.

This extension of the theory, on the other hand, does not imply that all compounds hitherto quinonoidally formulated should have polar structure; but the ideas advanced here bring out clearly that many types of what has been called quinoidation are possible. The group $(C_6H_5)_3C$ thus

forms three different types, the cation $(C_6H_5)_3C^+$, the free radical, and the anion $(C_6H_5)_3C^-$, which is present in the alkali metal compounds.

The rearrangement taking place when triarylmethyl chloride is transformed into the free radical is probably not polar at all and it may be rather closely related to the rearrangement taking place when hydroquinone is oxidised to quinone in which case the two oxygen atoms in the first moment may be considered univalent, a free radical being thus formed which is instantly transformed into the more stable configuration called the quinone structure.

After this paper was completed, a very interesting paper by W. MADELUNG¹ has appeared, dealing among other things with compounds showing halochromism. From an entirely different point of view and expressed in a different way he arrives at essentially the same conclusions. His "sextett carbon" is congruent with what I call "electronically divalent" carbon. His formulations of the violet aurine anion and the crystal violet cation are identical with mine. He, also, parallellises the nitrogen in indamine with carbon in the halochromic triaryl carbinol salts. His concept of "septett carbon" in the benzene rings (and the methyl carbon atom in triaryl methyls) may be useful, although the characteristics of the benzene ring remain just as puzzling as before. The electro-isomerism is extremely convenient in picturing the anion halochromism as shown by nitroso- and nitrophenols and the tautomeric behaviour of e. g. nitrosophenol towards alkylating agents.

¹ Zeitschr. für Elektrochemie 37, 197 (1931).

