[Contribution from the Chemical Laboratory of the University of California.]

COLOR CHANGES AMONG DYES OF THE TRIPHENYLMETHANE SERIES AS INFLUENCED BY THE HYDROGEN ION CONCENTRATION OF ACIDS OF DIFFERENT DISSOCIATION CONSTANTS.

(ON CATALYSES WITH WEAK ACIDS, III.[1])

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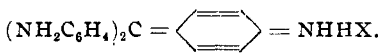
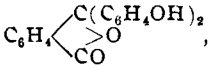
As is well known, the commonly accepted interpretation of the production of color in derivatives of triphenylmethane is the formation of a quinoid complex. Thus, colorless pararosaniline, the carbinol form $(NH_2C_6H_4)_3C(OH)$, in the presence of an acid, is transformed to the dye, the quinoid form

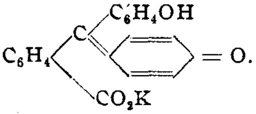


In like manner colorless phenolphthalein, the benzenoid form



$$C_6H_4\left\langle\begin{matrix} C(C_6H_4OH)_2 \\ >O \\ CO \end{matrix}\right. ,$$

in the presence of an alkali yields the colored quinoid form



In this molecular readjustment there is a certain resemblance to the rearrangement occurring in the transformation of the cinchona alkaloids, such as cinchonine, into their corresponding toxins. In the latter case there is a change from the carbinol to the ketone form with the shifting of hydrogen to a nitrogen atom;[2] in the former case there is a change from the carbinol to the quinoid form with a preliminary shifting of hydroxyl or acid radical to an amide group. In view of the peculiar catalyzing influence of the slightly dissociated organic acids in accelerating the speed of the conversion of cinchonine into cinchotoxine, it becomes of interest to determin whether relations in any way similar to these obtain among the derivatives of triphenylmethane in the conversion of the benzenoid into the quinoid form. From the nature of the change it seemed not unreasonable to suppose that phenomena of a somewhat similar character would be found among these derivatives, although probably modified by other reactions which do not obtain among the cinchona alkaloids.

Some months ago I began a study of a number of the dyes of the triphenylmethane series with reference to determining the influence of

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[1] Biddle, *Science*, 32, 486 (1910); *Ber.*, 45, 526, 2832 (1912); This Journal, 34, 500 (1912).

[2] Biddle, This Journal, 34, 500 (1912).

different concentrations of H ion as presented in acids of varying dissociation constant upon the speed of the conversion of the benzenoid or colorless form into the quinoid or colored form. The results obtained reveal a remarkable resemblance in many ways between the action of such acids in this case and their catalyzing action in the case of the cinchona alkaloids. While the investigation is incomplete, the facts developed are of sufficient interest to warrant their presentation at this time and to indicate some of the directions in which the study is being continued.

Fuchsine Sulfurous Acid.—Magenta decolorized by sulfurous acid since its first use by Schiff and Caro,[1] has become a well known and general reagent for the detection of aldehydes. As is known, the production of color in the presence of an aldehyde is not immediate and furthermore the sensitiveness of the reagent is diminished in the presence of strong mineral acids. The tint of the final color produced is also somewhat different in the presence of considerable excess of mineral acid, but is, on the other hand, not largely altered in intensity.

The complicated nature of the reactions probably involved in this reaction in some ways renders it unsuitable for this particular study. At the same time the production of color in the action of aldehydes without question involves the conversion of the benzenoid to the quinoid complex, and in this respect the speed of the reaction is worthy of consideration. Furthermore, the fact that the final color produced under like conditions differs little in intensity and tint, even in fairly concentrated solutions of the strong mineral acids, renders the study of the speed of the reaction a matter comparatively simple.[2]

A study of the speed of the production of color in the case of fuchsine sulfurous acid, in the presence of acids of varying dissociation constants, reveals a catalytic action of *almost exactly the same type* as that observed in the conversion of cinchonine into cinchotoxine. The speed of the formation of color increases with acids of decreasing dissociation constant and decreases with those of increasing dissociation constant. Thus, in the presence of excess of organic acids, such as acetic and propionic, the color appears in a few moments, whereas in the high hydrogen ion concentration afforded by excess of such acids as hydrochloric, all appearance of color may be retarded from 30 to 60 minutes or even longer. These results may be shown in a roughly quantitative way by adding to a series of test tubes containing normal solutions of a number of acids, such as propionic, acetic, formic, tartaric, chloroacetic, etc., one cc. each

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[1] Schiff, *Ann.*, **140**, 131: Meyer, *Ber.*, **13**, 2342 (1880); Tiemann, *Ibid.*, **14**, 791 (1881); Schmidt, *Ibid.*, **14**, 1848.

[2] The final color in the case of large excess of such an acid as hydrochloric has a distinct trend toward the violet.

of fuchsine sulfurous acid and after thoroughly shaking, two drops of a 1% solution of formaldehyde. It will be seen immediately that the deepening of color is most rapid with the acids presenting the lowest concentration of the hydrogen ion, and slowest with those most highly dissociated.

For an exact quantitative study of the velocity of the reaction, a Stammer colorimeter[1] was employed, the standard color for comparison being a solution similar to that tested, but which had stood until complete color change had been reached.

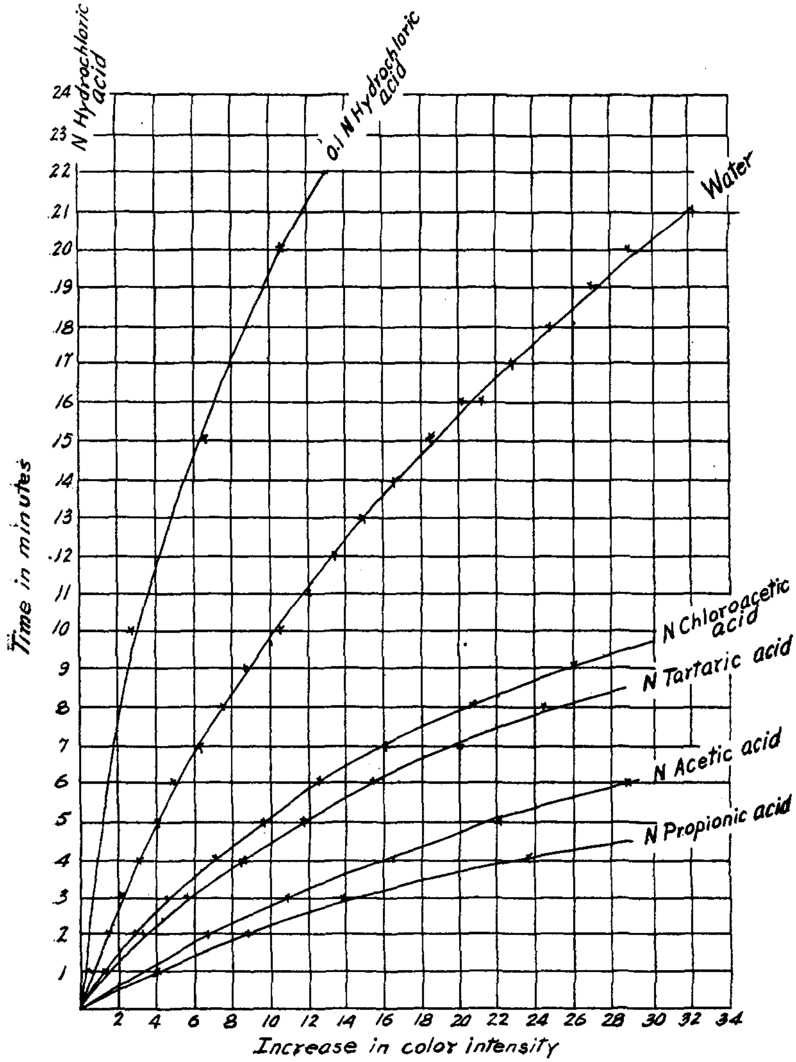

Fig. 1.

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[1] Franz, Schmidt and Haensch, Berlin.

In the experiments whose results are plotted above, in each case 10 cc. of the acid or water used were added to 1 cc. of the standard fuchsine sulfurous acid solution and then to this exactly ½ cc. of a 0.05% solution of ordinary 40% formalin. The temperature was approximately 18°. The changes in color intensity are plotted as abscissas and the successive time intervals as ordinates.

The comparison of color produced with that of the standard presents a little difficulty in the case of the strongly dissociated acids such as hydrochloric, on account of the fact that the initial tints with these acids have a pronounced trend toward the violet. This difficulty is in part met by using for comparison a color standard which contains hydrochloric acid.

The results, however, leave no question as regards the catalyzing action of the several acids studied (Fig. 1).

A consideration of the above results reveals the interesting fact that the velocity of the reaction increases with successive intervals of time—a result which points to the complexity of the reaction.

Indeed, as was called to my attention by Mr. E. Q. Adams, of this laboratory, after an inspection of the curve for the fuchsine sulfurous acid with water, the velocity is roughly proportional to the square of the time. We are, consequently, not dealing here with a reaction of the first order as is the case in the catalysis of the cinchona alkaloids[1] and as is apparently also the case, as will be shown further on, in the transformation of the carbinol base to the quinoid base in the triphenylmethane dyes.

In the case of the catalysis of the cinchona alkaloids, the speed of the conversion is, as has been shown,[2] a function of the molecular concentration of the weakly dissociated acid present. The speed of the color reaction with fuchsine sulfurous acid appears to be governed by somewhat similar conditions, increasing with the molecular concentration of the organic acid. This is shown in the following curves.

The fuchsine sulfurous acid reaction lends itself admirably as a lecture experiment to demonstrate the accelerating catalytic action of the slightly dissociated organic acids and the inhibiting action of the highly ionized mineral acids. If, for example, to a series of test-tubes containing 1 cc. of fuchsine sulfurous acid and equal volumes of the various acids (normal solutions) to be tested, there is added in each case an equal volume of a very dilute solution of formalin, the production of color and the depth of tint attained will be in inverse order to the dissociation constants of the acids studied.

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[1] The determination of the rate of this reaction in the case of the conversion of cinchonine (and cinchonidine) into cinchotoxine and of quinine (and quinidine) into quinotoxine has been made in this laboratory. The results of these determinations will be published shortly in THIS JOURNAL.

[2] *Ber.*, 45, 2836 (1912).

By proper dilution of the formaldehyde the rapidity of the reaction may be varied as desired.

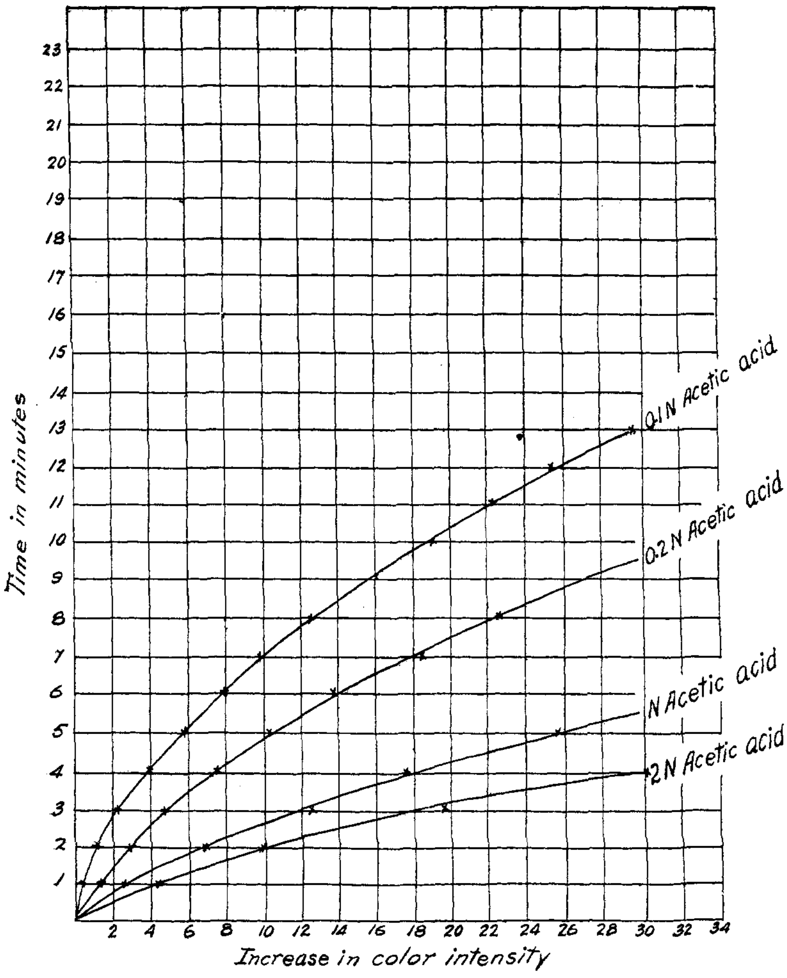
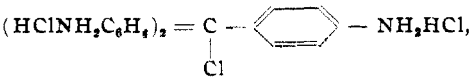


Fig. 2.

The Rosaniline Dyes in General.—The well known effect of the presence in excess of a highly ionized acid, such as hydrochloric in diminishing the intensity of color, and frequently as well the nature of the color, of a rosaniline dye, naturally leads one to infer that the conversion of the carbinol to the quinoid base would be inhibited in the presence of excess of such an acid. This inference is fully supported by experiment. If, for example, a few drops of a dilute solution of rosaniline carbinol are added to one cc. of *N* hydrochloric acid, the acid remains colorless, whereas the corresponding addition of the carbinol base to one cc. of *N* acetic acid speedily gives rise to the characteristic rosaniline color. This inhibition on the part of the highly ionized acid is doubtless due to the maintenance, in part, of the benzenoid form through the addition of a fourth molecule of the acid, thus leading to the colorless compound,



$$(\mathrm{HClNH_2C_6H_4})_2 = \underset{\displaystyle \mathrm{Cl}}{\mathrm{C}} - \mathrm{C_6H_4} - \mathrm{NH_2HCl},$$

a class of substances which has been studied by Rosenstiehl[1] and others.

In the action of an excess of any acid on a rosaniline dye or its carbinol base, the final condition of the reaction is without doubt one of equilibrium between the benzenoid or colorless form and the quinoid or colored form, and in this equilibrium, in any case, the ratio of the two forms to each other, other things being equal, is largely dependent on the concentration of the hydrogen ion of the acid present.

Furthermore, as has been shown by a number of investigators, the change from benzenoid to quinoid form and *vice versa* is not an instantaneous one but usually involves an appreciable element of time. This condition of equilibrium and the time element involved in reaching such equilibrium is clearly shown in the following experiments:

If to two test tubes containing, the one 0.1 *N* hydrochloric acid (1 cc.) and the other 0.1 *N* acetic acid (1 cc.) there is added the same quantity of rosaniline carbinol base (two drops of a dilute solution in each case), the hydrochloric acid remains practically colorless, while the acetic acid soon becomes deep red. If, after a few minutes, the acid condition in the two solutions is rendered the same by adding 0.1 *N* acetic acid (1 cc.) to the colorless hydrochloric acid and 0.1 *N* hydrochloric acid (1 cc.) to the colored acetic acid, it will be found that the colorless solution is but slightly affected and the colored solution (aside from the assumption of a slight violet tint) is at first unchanged. Gradually, however, the color fades and after the lapse of 40 to 60 minutes the two solutions present exactly the same appearance.

The shifting of equilibrium and the time element involved is shown in the effect of change of temperature on the production of color. Rise of temperature leads to the formation of the quinoid or colored form. If, for example, to normal solutions of such acids as formic, tartaric, chloroacetic and hydrochloric, there is added a little carbinol base, either of rosaniline or methyl violet (a few drops of dilute solution to 2–4 cc. of acid), the attainment of color equilibrium is in all cases gradual. If now one-half of each solution is warmed to 90°, it becomes highly colored in the case of all the acids mentioned, and when cooled the color only gradually fades back to the condition of equilibrium. After some time, how-

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[1] Baeyer and Villiger, *Ber.*, **37**, 598 (1904).

ever (usually 40–60 minutes), the color intensity in the case of any one acid is found to be the same in the heated and the unheated solutions.

Preliminary experiments with normal solutions of organic acids of varying dissociation constant, to which have been added one or two drops of a dilute solution of the carbinol base either of rosaniline or methyl violet, show that the speed of the production of color is greatest in the case of the acids presenting the lowest concentration of hydrogen ion.

From what has been said, however, it will readily be seen that a study of the speed of the conversion of a carbinol base of this series of dyes into the quinoid form in the presence of acids of varying concentration of hydrogen ion more properly resolves itself into a study of the speed of approach to the final condition of equilibrium in any case. In the action of excess of different acids on the carbinol base of such dyes as rosaniline, methyl violet and the like, both the quality and the intensity of the color finally reached in equilibrium vary greatly with the particular acid employed. This necessitates the comparison of the rate of color change in the case of any acid with the equilibrium effect produced under like conditions by that particular acid.

In the experiments whose results are plotted below, a preliminary measurement was made of the speed of approach towards equilibrium in the case of a very dilute solution of the carbinol base of methyl violet in the presence of acetic and of chloroacetic acids. The results obtained indicate that the speed of approach to the condition of equilibrium increases under the influence of acids presenting low concentrations of hydrogen ion and decreases under like influence of acids presenting high concentration of hydrogen ion. The carbinol base was prepared by addition of ammonia to a solution of ordinary methyl violet and a very little of the colorless base obtained was dissolved in water-alcohol containing a trace of ammonia to prevent reversal to the quinoid form. The color standard was prepared in the case of each acid by adding from a buret 5 cc. of the carbinol solution to 50 cc. of the given acid. Equilibrium was assured by heating one portion of each solution and allowing heated and non-heated portions to stand until both were of the same intensity of color. The acetic acid solution was violet in color; the chloroacetic, blue. In the experiment in each case, to 10 cc. of acid was added exactly 1 cc. of the carbinol solution, care being taken to agitate the acid during the addition of the carbinol base. The measurements were made as before at 18° in a Stammer colorimeter, the tube containing the solution being 50 cc. in length.

The colorimetric measurements lend themselves to a study of the order of a reaction of this type. If we assume that the depth of color in a 50 mm. column of the solution in which equilibrium has been reached represents complete change,[1] the readings of the colorimeter in mm. naturally give the part converted into the quinoid form. These readings may, consequently, be used in calculating a velocity constant to determin the order of the reaction.

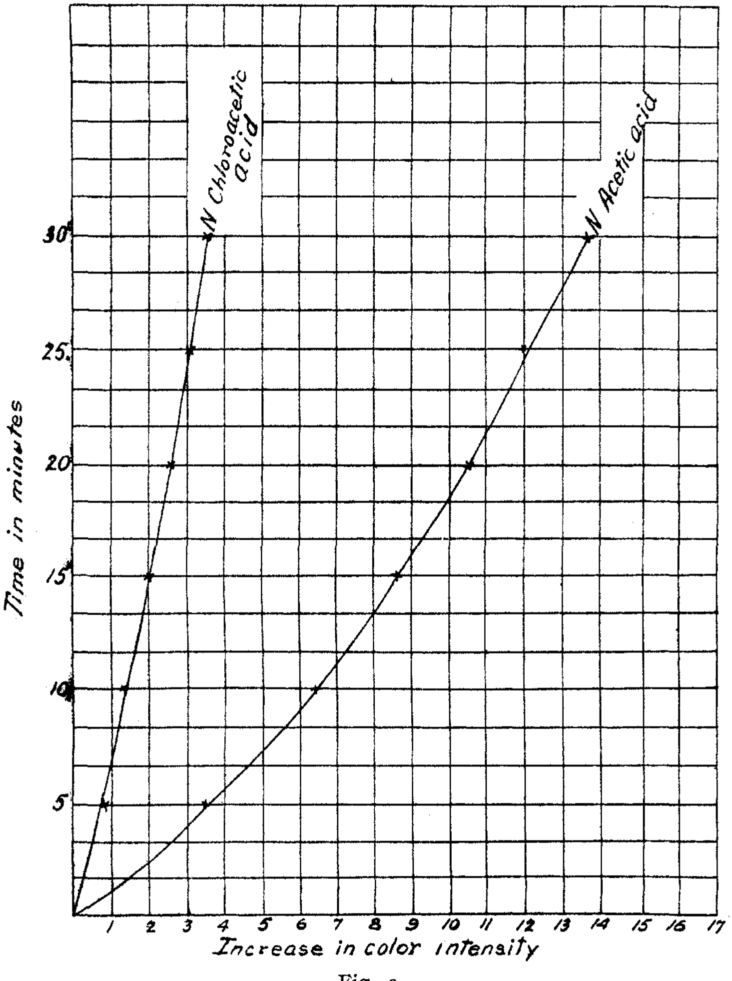

Fig. 3.

In the following preliminary determination, 2 cc. of the carbinol base of methyl violet were employed instead of 1 cc. as before. The value of K as calculated from the equation, $K = 1/t \log a/a - x$, points, as is seen, to a reaction of the first order:

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[1] The error introduced by this assumption in the case of acetic acid is small since the composition of the equilibrium mixture probably corresponds to more than 75% conversion and since we deal only with that part of the reaction in which the % of change is small.

t. Minutes.	Depth of color in mm., *i. e.*, x.	$a - x$.	K.
0	0	50.0	
1	3.4	46.6	0.0306
2	6.1	43.9	0.0282
3	9.0	41.0	0.0291
4	11.5	38.5	0.0284
5	13.9	36.1	0.0283
6	16.6	33.4	0.0292
7	18.3	31.7	0.0282

These results do not accord with those of Müller,[1] who, by conductivity measurements, finds the reverse transformation, *viz.*, the conversion of the quinoid into the benzenoid form, to be a reaction apparently of the second order.

The study of these color changes in derivatives of the triphenylmethane series and related series is being continued. Dyes of both the basic and acid type are being investigated to learn how general the phenomenon is with which we are dealing. It is of interest further to determin whether the speed of the reaction is a function *solely* of the diminishing concentration of the hydrogen ion or whether, as appears to be the case in the conversion of the cinchona alkaloids into their toxins, it is dependent also upon the nature of the acid (or possibly in the case of the acid dyes, the base) employed.

I shall appreciate it if, for a short time, I may be permitted to reserve the several lines of investigation here indicated.

Summary.

1. The resemblance between the molecular rearrangement of the cinchona alkaloids to their toxins and the conversion of a benzenoid to a quinoid form among the derivatives of triphenylmethane leads one to anticipate finding similar catalytic phenomena governing the velocity of the reaction in the two cases.

2. The speed of the production of color in the case of fuchsine sulfurous acid with an aldehyde increases in equivalent solutions with acids of decreasing dissociation constant and is retarded by acids, such as hydrochloric, which present a high concentration of the hydrogen ion.

The speed of the reaction appears, furthermore, to increase with the molecular concentration of an organic acid, such as acetic.

3. The speed of the conversion of a rosaniline carbinol base to the quinoid dye in its approach towards a condition of equilibrium between benzenoid and quinoid forms in the presence of a considerable excess of acid, apparently increases with decreasing dissociation constant of the particular acid employed (particularly studied was methyl violet in the presence of acetic and chloroacetic acids).

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[1] *Ber.*, **43**, 2609 (1900).