Statutes were proposed for the affiliation of the International Committee on Atomic Weights with the International Council.

As the International Council of Chemical Societies now has funds of its own, the expenses of the meeting no longer fall on the individual societies forming the Association.

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

THE INFLUENCE OF HYDROGEN ION AND OF NEUTRAL SALTS UPON COLOR CHANGES AND REACTION VELOCITIES AMONG DYES OF THE TRIPHENYLMETHANE SERIES.

(ON CATALYSES WITH WEAK ACIDS, V.)

By H. C. Biddle.

Received October 7, 1913.

1. Introductory.—As I have shown,[1] the speed of the assumption of color in the well-known magenta test for aldehydes, in the presence of excess of weak acids, closely resembles the conversion of the cinchona alkaloids into their toxins under like conditions. Thus the speed increases with acids of decreasing dissociation constant and decreases with acids of increasing dissociation constant. Furthermore the speed of the conversion increases in the presence of a weak acid, such as acetic, with the molecular concentration of the acid. Here, as in the case of the cinchona alkaloids, at least two factors apparently enter into the reaction—the inhibiting influence of the H^+ ion on the one hand and the accelerating influence of the molecule of the organic acid on the other.

The study of this catalysis was extended from the more complicated magenta reaction to the less involved conversion of a triphenylmethane dye from the colorless to the colored form, attention having been confined to the behavior of methyl violet in the presence of chloroacetic and acetic acids. Here, as in the case of the magenta reaction, the speed of conversion of the benzenoid to the quinoid form, in the approach toward a condition of equilibrium between the two forms, was found to be greater in the presence of the acid of lower dissociation constant. Subsequent study has shown that this law is general in its application to similar dyes of the triphenylmethane series, the reaction rate being a function, as will appear later, of the diminishing concentration of the H^+ ion. Thus, for example, rosaniline, para-rosaniline, malachite green and methyl violet all exhibit the same general phenomenon with normal solutions of such acids as chloroacetic, acetic, propionic etc., the speed of the reaction increasing with acids of decreasing dissociation constant.

In the previous paper on this catalysis[2] the question was raised, as to whether the speed of this reaction is a function *solely* of the diminishing

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[1] This Journal, 35, 273 (1913).

[2] Biddle, This Journal, 35, 281 (1913).

concentration of the H^+ ion, or whether, as is the case in the conversion of the cinchona alkaloids into their toxins, it is dependent also upon the nature of the acid employed. The experimental results lead to the former conclusion. In the catalysis of the rosaniline dyes as in that of the cinchona alkaloids, the speed of the reaction is conditioned upon the diminishing concentration of the H^+ ion,[1] but unlike the latter case it is not a function of the molecular concentration of the organic acid.[2] In the case of the dye, indeed, the speed of the conversion from the benzenoid to the quinoid form not only does not increase with increasing concentration of acid, but actually decreases under such conditions.

Furthermore, while in the case of the cinchona alkaloids diminution of the H^+ ion through addition to an organic acid of a salt with a common acid ion exerted but a slight effect,[3] such an addition in the case of the color change enormously accelerates the speed of the reaction.

Variations in the concentration of the H^+ ion are found to produce not only an alteration in the speed of the reaction, but also an alteration in depth of color and in some cases a complete shift in color tint. The effect of such variations, in other words, is both static and dynamic. These variations in color tint correspond with the observations already made by Szyszkowski[4] and others in the case of certain dyes.

Not less interesting is the "neutral salt effect" in the presence of highly dissociated acids. Results are obtained here strictly comparable with those investigated by Arrhenius,[5] Euler,[6] Spohr,[7] Stieglitz,[8] Acree,[9] Kellogg[10] and others in the case of the inversion of cane sugar, hydrolysis of esters and similar reactions. In other words, the addition of foreign salts to solutions of equal concentration of acid produces an effect equivalent to that of increasing the concentration of the H^+ ion. In the case

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[1] This conclusion is fully in accord with the careful research of Sidgwick and his coworkers, which unfortunately I had until recently overlooked. In their investigations of reaction velocities in the case of brilliant green, malachite green and diaminotriphenylcarbinol in the presence of acids and alkalies, they call attention, in the action of acid upon the carbinol base, to the diminishing speed of the reaction with increasing concentration of acid, but they are unable to account for the phenomenon (Sidgwick and Moore, *Z. physik. Chem.*, **58**, 385 (1907); *J. Chem. Soc.*, **95**, 889 (1909). Sidgwick and Rivett, *Ibid.*, **95**, 899 (1909)).

[2] Biddle, *Ber.*, **45**, 2837 (1912). Biddle and Rosenstein, THIS JOURNAL, **35**, 425 (1913).

[3] Biddle and Rosenstein, THIS JOURNAL, **35**, 425 (1913).

[4] *Z. physik. Chem.*, **58**, 420 (1907).

[5] *Ibid.*, **1**, 110 (1881); **4**, 237 (1889); **31**, 197 (1899).

[6] *Ibid.*, **32**, 348 (1900).

[7] *J. prakt. Chem.*, [2] **33**, 270 (1886).

[8] *Am. Chem. J.*, **32**, 224 (1904); **34**, 1689 (1905); **39**, 177, 596, 720 (1908); THIS JOURNAL, **34**, 1689 (1912).

[9] *Am. Chem. J.*, **38**, 259, 489 (1907); **39**, 226 (1908); **41**, 474 (1909).

[10] THIS JOURNAL, **31**, 403, 886, 889 (1909); **35**, 396 (1913).

of the inversion of cane sugar and the hydrolysis of esters, this leads to only one result—an increase in the speed of the reaction. In the case of the rosaniline dyes, however, such addition produces, as does variation of the H^+ ion, a static as well as a dynamic effect.

The static effect of the H^+ ion and of neutral salts upon phenolphthalein has been made the subject of careful study by Rosenstein[1] in his investigation of the ionization constant of the indicator.

2. The Speed of the Reaction, a Function of the Diminishing Concentration of the H^+ Ion.—As we have noted in the case of the cinchona alkaloids, both the nature of the acid and the concentration of the H^+ ion functionate in the catalysis to the toxins. In the color change of the triphenylmethane dyes, on the contrary, the speed of the reaction is a function of the diminishing concentration of the H^+ ion *without regard to the nature of the acid.* This is clearly shown in comparing the behavior of these dyes in the presence of acids of widely different nature, such as acetic and hydrochloric acids. In isohydric solution of the two acids, the dye exhibits the same color tint.

The alteration in tint and color with varying concentration of H^+ ion is very noticeable in the case of methyl violet, where, with diminishing concentration of hydrochloric acid, the color will shift from yellow through green, blue, blue-violet to rose-violet. Since isohydric solutions of different acids effect the same color change, one is led to suspect that the speed of the assumption of color, in the conversion of the carbinol base to the quinoid dye, will be found to be intimately associated with the diminishing concentration of the H^+ ion, and will be at the same time largely independent of the nature of the acid employed. This probability is fully confirmed by experiment. In isohydric solutions of hydrochloric and acetic acids, indeed, the speed of the conversion of the colorless into the colored form of the dye, in approaching the condition of equilibrium, is *identical.* The speed of the catalysis,[2] consequently, differs from that of the cinchona alkaloids in that it is independent of the *nature* of the particular acid employed.

3. The Relation of the Speed to the Diminishing Concentration of the H^+ Ion.—In the tables given below are presented the data representing the relation between speed of transformation and concentration of the H^+

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[1] Rosenstein, This Journal, 34, 1117 (1912).

[2] If, according to the suggestion of Ostwald, the term catalysis is employed to signify the acceleration or retardation of a chemical reaction by substances which themselves undergo no permanent change as a result of their reaction, a question may be raised as to the legitimacy of using the term in this case, since in this reaction, without doubt, H^+ ion enters into the reaction in the formation of ions of a mono-, di- and tri-acid base. In the light, however, of other phenomena which will be considered in a later paper, it seems well for the present to employ the term in the consideration of this reaction.

ion in the case of methyl violet, in the presence of hydrochloric acid of varying concentration. The method of procedure in the experimental determination, which, with slight modifications as to amounts, applies equally well to rosaniline, pararosaniline, or malachite green, was as follows:

A standard solution of the carbinol base was prepared by adding to a mixture of 200 cc. of water and 200 cc. of absolute alcohol, 20 cc. of a 0.1% solution of methyl violet and to this in turn sufficient caustic potash to produce complete decolorization of the solution on standing (14 cc. of a 0.5 *N* KOH solution were used). The color standard was prepared, in the case of each strength of acid, by adding from a buret 10 cc. of the carbinol solution to 50 cc. of the acid, the resulting solution being permitted to stand in each case until equilibrium color had been reached. In each solution prepared for testing, exactly 2 cc. of the carbinol base were added to 10 cc. of acid, care being taken to thoroughly agitate the acid during the addition. The alkali content of the standard carbinol solution was determined by titration[1] and the acid neutralized by the base contained in the 2 cc. of this solution was deducted in each case from the acid present. The free acid is assumed in each case to be completely dissociated and to occupy the actual volume resulting from the addition of the carbinol base (2 cc.) to the acid (10 cc.), or 12 cc. in all. If the methyl violet base is regarded as pentamethyltriaminotriphenylcarbinol, its concentration in the final solution is approximately 0.00002 molal. The measurements were made as before[2] at 19.5°(±0.2°) in a Stammer colorimeter, the tube containing the solution studied being 50 mm. in length. Each reading is, in general, the mean obtained from two successive determinations.

Although the colorimetric method does not lend itself to high accuracy of measurement, the results obtained are sufficiently definite to give us clear information regarding the influence of the H^+ ion. The speed of the reaction, while diminishing slightly in some cases with successive intervals of time, is apparently that of a reaction of the first order with respect to the color base.

Consequently:

$$dx/dt = K(a - x).$$

Integrating:

$$K_1 = 1/t \log a/a - x,$$

or

$$K_2 = 1/t_2 - t_1 \log a - x_1/a - x_2.$$

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[1] The base in the carbinol solution was determined by adding phenolphthalein to a measured volume and titrating with 0.005 *N* HCl until color had just disappeared. With care, a colorless end point is obtained which does not show the color of methyl violet until after the lapse of a short time.

[2] Biddle, THIS JOURNAL, 35, 279 (1913).

TABLE I.

Concentration of free hydrochloric acid .... 0.0375 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
5	5.4	44.6	0.00993	0.00993
10	9.4	40.6	0.00904	0.00816
15	13.3	36.7	0.00895	0.00877
20	16.5	33.5	0.00869	0.00792
25	19.6	30.4	0.00864	0.00843
			Mean, 0.00905	0.00864

TABLE II.

Concentration of free hydrochloric acid .... 0.0055 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
5	7.4	42.6	0.01391	0.01391
10	13.3	36.7	0.01343	0.01295
15	17.7	32.3	0.01265	0.01109
20	21.5	28.5	0.01221	0.01087
25	24.9	25.1	0.01197	0.01103
			Mean, 0.01283	0.01197

TABLE III.

Concentration of free hydrochloric acid .... 0.0033 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
5	8.5	41.5	0.01618	0.01618
10	14.9	35.1	0.01536	0.01455
15	20.7	29.3	0.01547	0.01569
20	24.9	25.1	0.01497	0.01344
			Mean, 0.01549	0.01496

TABLE IV.

Concentration of free hydrochloric acid .... 0.00216 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	$a - x$.	K_1.	K_2.
0	0.0	50.0	...	...
2	7.3	42.7	0.03427	0.03427
4	12.9	37.1	0.03239	0.03053
6	17.8	32.2	0.03185	0.03076
8	21.9	28.1	0.03128	0.02957
10	25.5	24.5	0.03098	0.02977
			Mean, 0.03215	0.03098

TABLE V.

Concentration of free hydrochloric acid.................. 0.00155 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K_1.	K_2.
0	0.0	50.0	...	...
2	11.2	38.8	0.05507	0.05507
4	19.3	30.7	0.05296	0.05085
6	25.7	24.3	0.05228	0.05077
8	30.8	19.2	0.05195	0.05115
10	34.5	15.5	0.05086	0.04648
			Mean, 0.05262	0.05086

TABLE VI.

Concentration of free hydrochloric acid.................. 0.00095 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K_1.	K_2.
0	0.0	50.0	...	...
1	13.6	36.4	0.13787	0.13787
2	22.7	27.5	0.13140	0.12494
3	28.9	21.1	0.12489	0.11188
4	34.1	15.9	0.12439	0.12288
5	37.5	12.5	0.12041	0.10448
6	40.7	9.3	0.12175	0.12843
			Mean, 0.12678	0.12175

TABLE VII.[1]

Concentration of free hydrochloric acid.................. 0.00034 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i e.*, *x*.	*a* — *x*.	K_1.	K_2.
0	0.0	50.0	...	...
1	40.0	10.0	0.69897	0.69897
2	47.5	2.5	0.65052	0.60206
			Mean, 0.67474	0.65051

These experimental results are given in Figs. 1 and 2, the speeds, $K_1 \times 10^3$, being plotted as abscissas and the molal concentrations of the H^+ ion[2] $\times 10^4$ being plotted as ordinates. The graphs in the two figures

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[1] The reaction is so rapid at this low concentration of H^+ ion that it is difficult to obtain accurate readings. The experimental error is consequently larger in this case than in the others.

[2] Since 0.0375 molal hydrochloric acid is dissociated to the extent of approximately 97.5%, the assumption of complete dissociation at this concentration introduces a negligible error in plotting the curve. In all the experiments the influence upon the ionization by the alcohol introduced from the methyl violet solution (about 1 vol. in 12 vol.) is ignored. It may be noted, however, that the ratio between the alcohol and the remainder of the solution is in all cases the same.

are the same, that in Fig. 2 being on a scale sevenfold larger than that in Fig. 1.

A consideration of this curve is of some interest. It shows very clearly that while the speed of the reaction in approaching the condition of equilibrium is a function of the diminishing concentration of the H$^+$ ion, it is not a *linear* function of that value. Between the limits of 3.75 × 10^{-2} and 5.5 × 10^{-3} molal concentration of H$^+$ ion, the speed[1] of the color change varies but slightly with varying concentration of the H$^+$ ion. Below the latter value the speed experiences a rapidly progressive increase until, at concentrations of the H$^+$ ion varying from 1.55 × 10^{-3} to 3.4 × 10^{-4} molal, the increments of speed with succeeding decrements in the concentration of the H$^+$ ion become enormous.

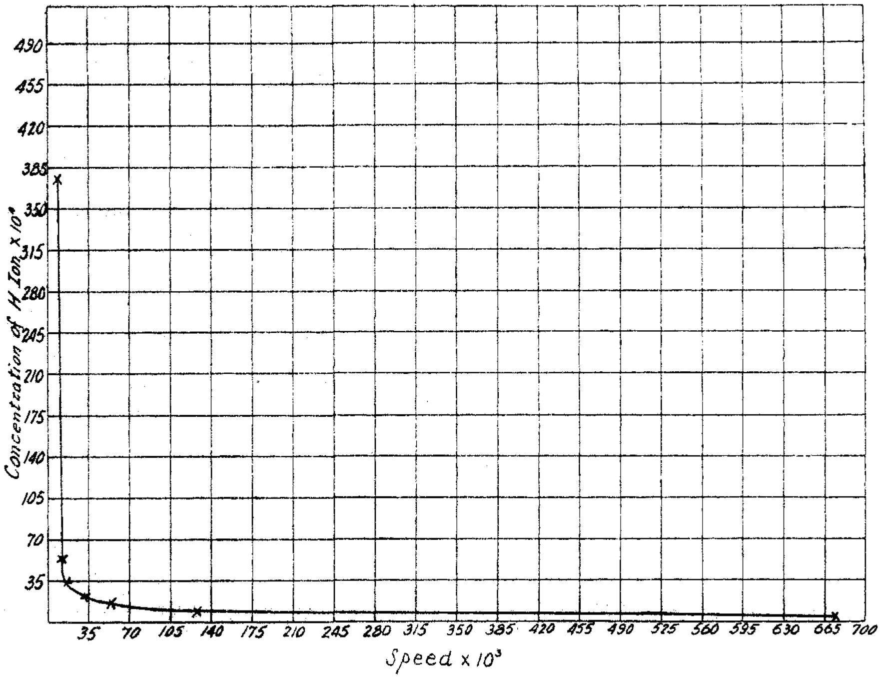

Fig. 1.

The complexity of this curve precludes the possibility of the speed

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[1] It is to be noted that in comparing the speeds of approach to a condition of equilibrium in each case, we are not comparing the speeds of approach to a *common* depth of color. Since slight variations in concentration of the H$^+$ ion alter the color tint, it becomes impossible to make the latter comparison with any degree of accuracy. In general the color of the equilibrium color standard becomes lighter with increasing concentration of H$^+$ ion. The result is that if the speed values could be reduced to those of approach to a common depth of color, the variations in speed with varying concentration of H$^+$ ion would be somewhat greater than those observed, since the low values would then become lower and the high values higher.

of the reaction being expressed as any simple function of the concentration of the H$^+$ ion. Interestingly enough, however, the speed of the reaction appears to be a linear function of the square of the concentration of the OH$^-$ ion. If, for example, the reciprocal of the concentration of the H$^+$ ion is represented by y and the values of $y^2 \times 10^{-4}$ are plotted as ordinates, while the speeds $\times 10^3$ are plotted as abscissas, the graph given in Fig. 3 is obtained. Discarding the value taken from Table VII, because of the necessary inaccuracy of measurement in this case, the speed, within the limits of experimental error, appears to be a linear function of y^2.[1]

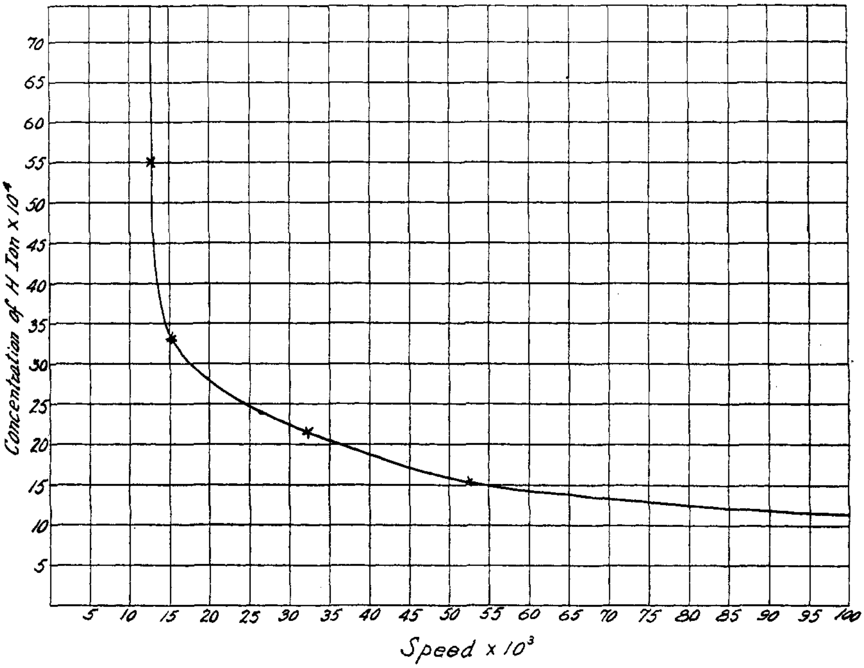

Fig. 2.

4. *The Influence of Change of Temperature upon the Speed of the Reaction.*—The speed of the conversion of the carbinol base into the quinoid dye varies to a considerable extent with changes in temperature, the speed in general increasing with rising temperature. Such an effect is in accord with the results obtained by Noyes[2] as to the decreasing dissociation of an acid with rise of temperature, but can scarcely be attributed solely to this cause.

The variations in speed with slight changes in temperature are found

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[1] In this connection I wish to thank Prof. G. N. Lewis of this department for calling my attention to this interesting relation after he had considered the data given above.

[2] A. A. Noyes, This Journal, 30, 346 (1908).

to be slight in the region in which alterations in the concentration of the H^+ ion produce little variation in the velocity of the reaction, but become very large in the region in which such variations are accompanied by marked changes in speed. Thus in concentrations of H^+ ion ranging from 3.75×10^{-2} to 5.5×10^{-3} molal a few degrees change of temperature produce but slight effect as compared with similar alterations within the range of concentration varying from 2×10^{-3} to 3.4×10^{-4} molal. A few degrees rise of temperature within the latter range increases the speed greatly. This is clearly shown in the following case with dilute hydrochloric acid, where a rise of roughly 4° increases the speed of the reaction almost 50%.[1]

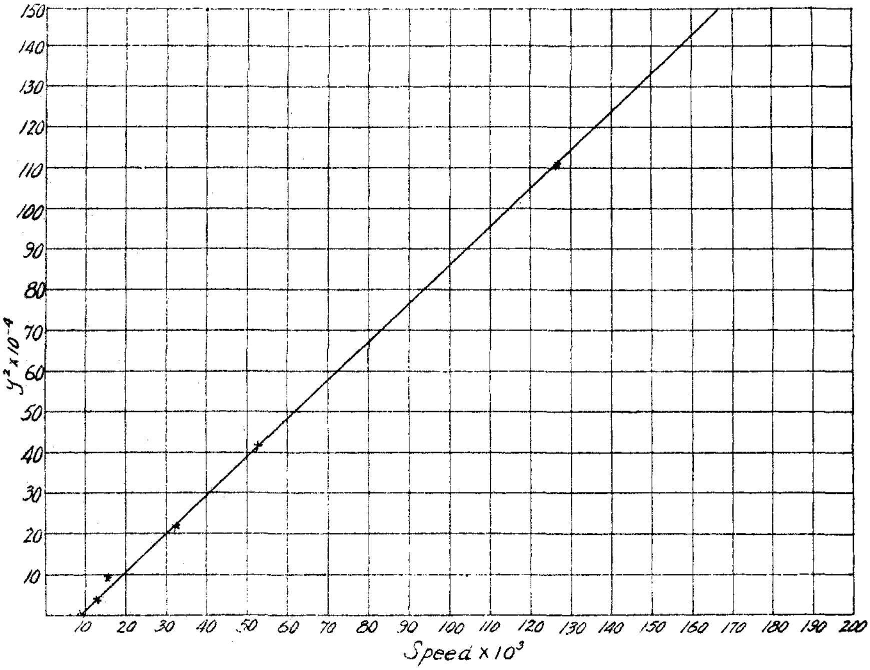

Fig. 3.

TABLE VIII.

Concentration of free hydrochloric acid .... 0.00176 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K_1.	K_2.
0	0.0	50.0	...	...
2	10.5	39.5	0.05118	0.05118
4	18.5	31.5	0.05017	0.04914
6	24.7	25.3	0.04931	0.04760
8	30.0	20.0	0.04974	0.05104
		Mean,	0.05010	0.04974

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[1] A careful study of this temperature effect is in progress in this laboratory.

TABLE IX.

Concentration of free hydrochloric acid.................. 0.00176 Molal.
Temperature... 23.5°(±0.5°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K₁.	K₂.
0............	0.0	50.0	...	...
2............	15.0	35.0	0.07745	0.07745
4............	24.6	25.4	0.07353	0.06962
5............	28.5	21.5	0.07331	0.07240
6............	32.0	18.0	0.07395	0.07716
		Mean,	0.07456	0.07415

5. Variations in Speed through the Addition of Salts.—The influence of the H^+ ion upon the speed of this catalysis naturally leads to a study of the effect of varying the concentration of this ion in solutions of uniform concentration with respect to the acid employed. Such variation is easily produced by the addition of suitable salts to the solution. Decrease in the concentration of the H^+ ion is of course readily effected in the case of a weak acid by the addition of a highly dissociating salt with a common acid ion, and, as Arrhenius[1] has shown, increase in the concentration of the H^+ ion is produced in the case of such an acid by the addition of soluble foreign salts, it being of course understood that the salt added in the latter case is not that of a weak acid. In the study of the cinchona alkaloids the addition of a salt with a common acid ion was found to exert at most a slight, if not an inappreciable effect upon the speed of the catalysis.[2]

From the large variation in speed already noted in the conversion of the carbinol form of a rosaniline dye into its quinoid form with slight variation in the concentration of the H^+ ion, we would naturally expect in this case that in the presence of weak acids large variation in speed would be brought about by the addition of suitable salts. The expectation is fully realized. Addition of a salt with a common acid ion, for example, greatly accelerates the speed of the conversion. To such an extent may this be increased, indeed, that it may become almost instantaneous. On the other hand, addition of a salt, such as sodium or potassium chloride, greatly retards the speed of the conversion. Sufficient addition, indeed, may almost if not altogether inhibit the change. It is thus possible in the solution of a weak acid, such as acetic acid, to effect through the addition of different salts a variation in the speed of the conversion ranging wellnigh from zero to infinity.

In the determinations which are recorded below the speed of the conversion was measured in the case of normal acetic acid and in the case of normal acetic acid containing on the one hand sodium acetate and on

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[1] *Z. physik. Chem.*, 31, 197 (1899).

[2] Biddle and Rosenstein, THIS JOURNAL, **35**, 425 (1913).

the other sodium chloride. The concentrations of acid and salt represent the actual concentrations after the addition to 10 cc. of solution of 2 cc. of the methyl violet. The acid neutralized by the alkali in the methyl violet and the minute quantity of salt formed therefrom are, however, in these cases ignored.

TABLE X.

Concentration of free acetic acid........................ 0.833 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	$a - x$.	K_1.	K_2.
0...........	0.0	50.0	...	...
5...........	11.0	39.0	0.02158	0.02158
10...........	18.2	31.8	0.01965	0.01773
15...........	24.6	25.4	0.01832	0.01627
20...........	28.5	21.5	0.01833	0.01810
			Mean, 0.01947	0.01842

TABLE XI.

Concentration of free acetic acid........................ 0.833 Molal.
Concentration of sodium acetate........................ 0.00833 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	$a - x$.	K_1.	K_2.
0...........	0.0	50.0	...	...
1...........	8.0	42.0	0.07572	0.07572
2...........	12.9	37.1	0.06480	0.05388
3...........	18.5	31.5	0.06689	0.07106
4...........	22.4	27.6	0.06452	0.05740
5...........	25.7	24.3	0.06267	0.05530
			Mean, 0.06692	0.06267

TABLE XII.

Concentration of free acetic acid........................ 0.833 Molal.
Concentration of sodium acetate........................ 0.0833 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	$a - x$.	K_1.	K_2.
0...........	0.0	50.0	...	...
1...........	32.0	18.0	0.44369	0.44369
2...........	43.6	6.4	0.44639	0.44909
3...........	47.7	2.3	0.44575	0.44445
			Mean, 0.44527	0.44574

TABLE XIII.

Concentration of free acetic acid.......................... 0.833 Molal.
Concentration of sodium chloride.......................... 0.0833 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0...........	0.0	50.0	...	...
5...........	6.0	44.0	0.00910	0.00910
10...........	10.5	39.5	0.01023	0.00937
15...........	14.4	35.6	0.00984	0.00903
20...........	17.7	32.3	0.00948	0.00845
25...........	21.4	28.6	0.00970	0.01057
		Mean,	0.00967	0.00930

TABLE XIV.

Concentration of free acetic acid.......................... 0.833 Molal.
Concentration of sodium chloride.......................... 0.416 Molal.
Temperature.. 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, x.	$a - x$.	K_1.	K_2.
0...........	0.0	50.0	...	...
5...........	4.0	46.0	0.00724	0.00724
10...........	6.8	43.2	0.00635	0.00546
15...........	9.4	40.6	0.00603	0.00539
20...........	11.5	38.5	0.00567	0.00461
		Mean,	0.00632	0.00567

In the effect of neutral salts upon the speed of this catalysis it is of interest to raise the question as to whether or not the effect is due *entirely* to the varying concentration of the H^+ ion of the weak acid. In his research "Ueber die Änderung der Stärke schwacher Säuren durch Salzzusatz," in which he makes use of the speed of the inversion of cane sugar to determine the increase in the dissociation constant of a weak acid produced by the presence of a foreign salt, Arrhenius shows that the increase in the speed of the conversion is modified by two other conditions, *viz.*, (*a*) the formation of new electrolytes through double decomposition and (*b*) a direct effect of the neutral salt on the catalysis.[1]

In the conversion of the colorless form of a rosaniline dye into the colored form in the presence of a weak acid such as acetic acid and a salt of this acid such as sodium acetate, condition (*a*) could not arise, since no new electrolyte would be formed. In the retarding influence of a foreign salt, such as sodium chloride, however, new electrolytes would naturally be formed and (*a*) must be taken into consideration. In such a case the general effect as Arrhenius has shown would be to increase slightly the concentration of the H^+ ion.

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[1] *Z. physik. Chem.*, 31, 197 (1899).

The direct effect (*b*) of a neutral salt upon the catalysis must now be considered. This, *the "neutral salt effect" proper*, may be investigated by studying the influence of such a salt on the speed of the reaction in the presence of a dilute solution of a highly dissociated acid, such as hydrochloric acid.

As I have already pointed out (page 86) the color tint of the rosaniline dyes, such as rosaniline, malachite green and methyl violet, shifts with varying concentration of the H^+ ion. In the case of methyl violet this may lead to a complete change, the color in this case with increasing concentration of H^+ ion varying from rose-violet through blue to grass green and at higher concentrations to yellow. The general effect of increasing concentration of a chloride such as sodium chloride on a dilute solution of hydrochloric acid would naturally be to diminish somewhat the concentration of the H^+ ions. Under such conditions we should expect an alteration in color tint corresponding to such decrease. Interistengly enough, the color change is just the reverse. The alteration of color tint produced in a rosaniline dye in dilute hydrochloric acid by the addition of a chloride such as potassium, sodium or magnesium chloride is uniformly in the direction following an *increasing* concentration of the H^+ ion. Salts of similar highly dissociated acids such as the bromides and nitrates produce a similar effect, though not quite so pronounced in the case of the nitrates. Thus, in a 0.005 molal solution of hydrochloric acid, containing methyl violet of similar concentration to that used in the preceding experiments, increasing concentration of magnesium chloride will cause a variation of color from violet through blue to grass green, precisely as is effected by an increase in the concentration of the H^+ ion.

In view of these results it became of great interest to determine how the *speed* of the conversion of the colorless to the colored base would be affected under such conditions by the presence of a neutral salt. Direct measurements revealed the fact that the speed was indeed altered under such conditions, and that the alteration was in the same direction as that indicated by the shift of color tint. In other words, the presence of a chloride such as sodium chloride lessened the speed of the reaction. Furthermore, the speed of approach to a condition of equilibrium in the case of a given color tint was found to correspond with the speed observed in the case of the same color tint produced by definite increase in the concentration of hydrochloric acid. Thus, a solution containing 2 molal sodium chloride and 0.00176 hydrochloric acid showed less than $^1/_4$ the speed exhibited by the acid alone, giving an effect corresponding to an increase in the concentration of the H^+ ion of more than 200% and this in a solution of such dilution with respect to the acid, that the latter in the absence of the salt may be regarded as completely dissociated. These results are set forth in the following determinations:

TABLE XV.

Concentration of free hydrochloric acid .... 0.00176 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K₁.	K₂.
0	0.0	50.0	...	...
2	10.5	39.5	0.05118	0.05118
4	18.5	31.5	0.05017	0.04914
6	24.7	25.3	0.04931	0.04760
8	30.0	20.0	0.04974	0.05104
		Mean,	0.05010	0.04974

TABLE XVI.

Concentration of free hydrochloric acid .... 0.00176 Molal.
Concentration of sodium chloride .... 0.0416 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K₁.	K₂.
0	0.0	50.0	...	...
2	7.5	42.5	0.03529	0.03529
4	13.5	36.5	0.03417	0.03305
6	19.0	31.0	0.03460	0.03546
8	23.5	26.5	0.03445	0.03405
		Mean,	0.03462	0.03446

TABLE XVII.

Concentration of free hydrochloric acid .... 0.00176 Molal.
Concentration of sodium chloride .... 0.416 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K₁.	K₂.
0	0.0	50.0	...	...
5	8.6	41.4	0.01639	0.01639
10	15.5	34.5	0.01612	0.01584
15	20.4	29.6	0.01518	0.01331
20	25.0	25.0	0.01505	0.01467
		Mean,	0.01568	0.01505

TABLE XVIII.

Concentration of free hydrochloric acid .... 0.00176 Molal.
Concentration of sodium chloride .... 2.05 Molal.
Temperature .... 19.5°(±0.2°)

Time. Min.	Depth of color in mm., *i. e.*, *x*.	*a* — *x*.	K₁.	K₂.
0	0.0	50.0	...	...
5	7.4	42.6	0.01391	0.01391
10	12.5	37.5	0.01249	0.01108
15	16.5	33.5	0.01160	0.00980
20	20.0	30.0	0.01110	0.00959
		Mean,	0.01225	0.01109

In general the action of a neutral salt was found to diminish with increasing concentration of acid. Thus while the influence of sodium chloride upon the color and the speed of the reaction in a 0.0375 *N* hydrochloric acid solution is of the same general character as in the case of the diluter acid, the effect is much less pronounced. This is fully in accord with the observation made by Arrhenius[1] in the catalysis of sugar, etc., that neutral salts act more strongly in the presence of dilute acids than in the presence of those of higher concentration.

The behavior of sulfates in this catalysis is of interest as it seems at first glance not to correspond with that of the salts of the monobasic acids. In other words, the retarding effect does not appear in the case of neutral sulfates. Thus, the reaction velocity in 0.00176 *N* hydrochloric acid, containing 0.416 molal magnesium sulfate, was found to be 0.05018, or practically the same as that in the acid alone. The reaction velocity in 0.00176 *N* sulfuric acid alone at 20.7°(±0.2°) was found to be 0.05310; the reaction velocities at the same temperature in 0.00176 *N* sulfuric acid containing 0.416 molal magnesium sulfate and in the same acid containing 0.416 molal potassium sulfate were respectively, 0.06006 and 0.09100. The color tint in each instance corresponded with that previously observed in the case of like reaction velocities with varying concentrations of hydrochloric acid.

The abnormal behavior of sulfates in catalyses, in general as compared with that of the salts of the monobasic acids, has been observed by several investigators.[2] An explanation of the phenomenon is undoubtedly to be sought, as suggested by Euler, in the tendency of the neutral sulfate to form the acid sulfate under the conditions of the experiment and thus to effect a slight decrease in the acidity of the solution.

6. Discussion of the "Neutral Salt" Effect.—The behavior of neutral salts in the catalysis of the rosaniline dyes is a remarkable one. It corresponds in general, however, to the effect of such salts as observed by Arrhenius, Euler, Spohr, Stieglitz, Acree and others[3] in such catalyses as the inversion of cane sugar and the saponification of esters. While it seems wise, for the present, to defer full discussion of the results obtained until further quantitative data are secured, a brief consideration of some of the hypotheses advanced to account for the "salt effect" in general may not be out of place.

As was suggested in the investigations of Arrhenius and Euler[4] the salt acceleration in the case of such catalyses as the inversion of cane sugar is probably largely to be ascribed to an increased ionization of water as

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[1] *Z. physik. Chem.*, **4**, 239 (1889).

[2] Spohr, *Z. physik. Chem.*, **2**, 195 (1888). Euler, *Ibid.*, **32**, 355 (1900).

[3] See previous references.

[4] Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899); *Z. Electrochem.*, **6**, 10 (1900). Euler, *Z. physik. Chem.*, **32**, 348 (1900).

well as of other electrolytes in the presence of the neutral salt. This is possibly due, as Stieglitz[1] has emphasized, to an increase in the ionizing power of the solvent from the presence of the strong electrolyte.

This explanation is unquestionably a natural one and may possibly serve to account for the "salt effect" in the catalysis studied in this paper. In the determinations in which hydrochloric acid was used (see pages 88–89), the dilution was such that the acid may be regarded as almost completely ionized in the aqueous solution alone. The only electrolytes left for consideration (aside from the salt itself), are, consequently, the water and the dye.

Now, as regards the solvent, it may be noted that any moderate increase in the dissociation of water would not lead to a large increase in the concentration of the H^+ ion. And even though the effect of both H^+ and OH^- ions from such dissociation is in the direction of diminishing the speed of this reaction, it seems difficult to understand how alterations in the reaction velocity, corresponding to such an increase in the concentration of the H^+ ion (200% and more) above that of the acid present, can be caused solely by an increased ionization of water in the presence of electrolytes.

We are, consequently, led to consider the dye. As regards the methyl violet, it may be noted that the condition of equilibrium between carbinol and dye stuff is not a simple one. The three amine groups present the possibility of mono-, di- and tri-acid salts and these must all be taken into consideration in any equilibrium between carbinol and dye in the presence of excess of acid. While this is true, the effect of a heightened ionizing power of the solvent, through the influence of neutral salts, may possibly be safely regarded as producing an alteration in equilibrium between carbinol and quinoid forms equivalent to that resulting from an increase in concentration of H^+ ion.

Of interest in this connection is the effect of a neutral salt upon a neutral solution of a rosaniline dye. As I have already shown, the addition of a chloride such as sodium chloride to a solution of a dye of this series containing a little hydrochloric acid, causes a shift of color tint in the direction effected by an increase in the concentration of the H^+ ion.[2] Addition of such a salt to a *neutral* solution of such a dye does not apparently affect the color tint.

A number of investigators have suggested the possible formation of complex ions on the addition of salts; while Acree has called attention to the possible participation of the non-ionized salt in a catalysis.[3] That

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[1] Stieglitz, THIS JOURNAL, **32**, 224. "Qualitative Chem. Analysis," 1911, page 109.

[2] See also Szyszkowski, *Z. physik. Chem.*, **58**, 420 (1907).

[3] *Am. Chem. J.*, **48**, 365 (1912).

an undissociated electrolyte may act as a catalytic agent, I have, indeed, shown[1] in the case of the cinchona alkaloids, where the speed of the conversion is found to be a function of the molecular concentration of the undissociated organic acid. The experimental data are, however, as yet insufficient to enable us to pronounce upon the merits of either of these hypotheses as applied to the action of salts in this catalysis.

The hypothesis considered by Goldschmidt, and others,[2] in explaining the "neutral salt effect" regards a possible parallel action of ions and of undissociated molecules. This has been studied by Stieglitz in the case of the imido-esters. Such an hypothesis might be applied to the ionized and non-ionized molecule of the rosaniline dye, but here again the experimental data are insufficient to lead to any conclusion.

A possible factor in the salt effect, to which I believe attention should be called, is the increased mobility of the H^+ ion resulting from the presence of a salt. As shown by Nernst[3] and later developed by Planck[4] and by Pleijel[5] the diffusion constant of hydrochloric acid is found to increase in salt solutions of increasing salt concentration. However this may be accounted for, the resulting dynamic effect of this increase would naturally be a heightening of the activity of the H^+ ion.

7. The Speed of the Reaction as a Dynamic Method in Determining the Concentration of the H^+ Ion.—The action of a neutral salt in shifting the color tint of a dye as noted above, indicates how misleading the results may be in employing a colorimetric method such as that of Salm[6] in estimating under such circumstances the concentration of the H^+ ion in a solution, when no account is taken of the "salt effect." Even in the absence of salts, the static method of Salm leaves much to be desired from the standpoint of accuracy.

While subject to the same disturbing influence of neutral electrolytes, the speed of the conversion of the carbinol base into the quinoid dye naturally suggests itself as a kinetic method for measuring the concentration of the H^+ ion in the absence of appreciable quantities of salts. Although in no way presenting the wide range offered by the inversion of cane sugar or the saponification of an organic ester, nor possibly the accuracy, obtainable through the decomposition of diazo-acetic ester,[7]

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[1] Biddle, *Ber.*, **45,** 2832 (1912).

[2] Goldschmidt, *Z. physik. Chem.*, **70,** 627 (1910); **81,** 30 (1912); *Z. Elektrochem.*, **17,** 684 (1911). Bredig, *Z. Elektrochem.*, **18,** 535 (1912). Snethlage, *Ibid.*, **18,** 539 (1912). Acree and his coworkers, *Am. Chem. J.*, **48,** 353 (1912); **49,** 116, 127, 345, 369, 474 (1913). Stieglitz, THIS JOURNAL, **34,** 1689 (1912).

[3] *Z. physik. Chem.*, **2,** 613 (1888).

[4] Planck, *Wied. Ann.*, **40,** 56 (1890).

[5] Pleijel, *J. physik. Chem.*, **72,** 1 (1910).

[6] *Z. physik. Chem.*, **57,** 471 (1906).

[7] Bredig, *Verhandlungen des Naturhistorisch—Medizinischen Vereins zu Heidelberg, N. F.*, **9,** 1 (1907).

yet the ease with which measurements may be made invites a brief consideration of the possibilities presented.

A study of the graph in Fig. 2, as we have already noticed, reveals the fact that with H^+ ion concentrations greater than 5.5×10^{-3} molal, the variations in speed of the reaction with varying concentration of the H^+ ion are too slight to render them of any value in determining such concentrations with any degree of accuracy. On the other hand, variations of H^+ ion concentration within the range of 1.55×10^{-3} to 3.4×10^{-4} are accompanied by such marked increase in the speed of color change that, within this range, the latter might be employed to detect very slight variations in the former. Within this range, however, the speed experiences marked alteration with slight variations in temperature. Measurements for comparison, consequently, must be made at some fixed temperature, otherwise large error will be introduced.[1] The temperature effect becomes less in passing from 1.55×10^{-3} to 5.5×10^{-3} molal concentration of the H^+ ion, and within this range such concentration should be determined from the speed of the reaction with a fair degree of accuracy.

Within a limited range of concentration of H^+ ion, the speed of this color change may thus be used to determine the value of the concentration. Within this range, the degree of accuracy much exceeds any possibility presented by any static colorimetric scheme such as that worked out by Salm. Unfortunately, however, the range in the case of any one indicator is small. At the same time the possibility presents itself of extending this range through a careful study of a number of basic dyes such as rosaniline, pararosaniline, and malachite green on the one hand and of acid dyes such as phenolphthalein and thymolphthalein on the other. Work is being carried forward in this direction in this laboratory.

To determine something regarding the possible accuracy of this method in estimating the concentration of the H^+ ion, measurements were made of the speeds of reaction in a number of acid solutions and the calculated concentration of the H^+ ion was compared with that derived from the graphs of Figs. 1 and 2. The quantity of salt present in each case was too small to diminish, to any noticeable extent, the speed of the reaction through the "neutral salt effect." The degree of dissociation, a, of one gram-molecule of the weak acid in volume, V, in the presence of its salt was calculated from the equation, $a(a + nb)/(1 - a)V = K$, where n equals the number of gram-molecules of the salt with the degree of dissociation, b, in volume, V.[2] The potassium acetate formed by the

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[1] In the experimental determinations made in this paper temperature variations, amounting to ±0.2° are allowed for, although in many cases the variation was less than this.

[2] Arrhenius, "Theories of Solutions," page 166.

TABLE XIX.

	Acid.	Salt.	Reaction velocity at 19.5°(±0.2°)C.	Concentration of H^+ ion from observed reaction velocity.	Calculated concentration of H^+ ion.
1.	Hydrochloric acid (0.00176 molal)........	Potassium chloride (0.00242 molal)	0.05010	0.00160 molal	0.00176 molal
2.	Acetic acid (0.8333 molal)...............	Potassium acetate (0.00268 molal)	0.02124	0.00272 molal	0.00282 molal
3.	Acetic acid (0.4166 molal)...............	Potassium acetate (0.00268 molal)	0.05401	0.00150 molal	0.00175 molal
4.	Acetic acid (0.2083 molal)...............	Potassium acetate (0.00268 molal)	0.07843	0.00105 molal	0.00125 molal
5.	Acetic acid (0.8333 molal)...............	Potassium acetate (0.00268 molal) Sodium acetate (0.00833 molal)	0.06540	0.00138 molal	0.00136 molal

alkali from the methyl violet in examples 2–5, is assumed in each case to be completely dissociated, while the minute quantity of acetic acid neutralized by the alkali in these cases is ignored (the error introduced by these assumptions is negligible). The sodium acetate added in example (5) is regarded as dissociated to the extent of 90%. Following are the results obtained:

Up to the present time the dyes of the triphenylmethane series which have been studied in this catalysis are those possessing two and three NH_2 groups. To determine the possible influence of the several NH_2 groups upon this reaction velocity the study is being extended to monaminotriphenylcarbinol and its derivatives.[1] In these simpler cases the complex conditions introduced by the formation of diacid (and triacid) salts will naturally be eliminated. The results obtained here will, we trust, throw further light upon the catalysis of the cinchona alkaloids, in which substances the elimination of the "quinoline nitrogen" or second nitrogen atom was not feasible without destroying the nature of the alkaloid complex.

Study is, furthermore, in progress in conjunction with Messrs. Ludwig, Rosenstein and L. Q. Adams, of this laboratory, with regard to the absorption spectra of solutions of a rosaniline dye containing increasing quantities of an acid, in the hope of securing fuller information as to the existence and nature, in the solution, of the mono-, di- and tri-acid salts of the dye.

Summary.

1. In the conversion of a rosaniline dye from the colorless to the colored form, the speed of the reaction in the approach to the equilibrium color is a function of the diminishing concentration of the H^+ ion.

2. The speed of the reaction, unlike that of the conversion of the cinchona alkaloids into their toxins, is independent of the nature of the acid present and is consequently not, as in the latter case, a function of the molecular concentration of the acid.

3. The speed of the reaction increases with rise of temperature, the rate of increase rising with diminishing concentration of the H^+ ion.

4. Neutral salts in diminishing or increasing the degree of dissociation of a weak acid correspondingly increase or diminish the speed of the reaction in the presence of such an acid.

5. The "neutral salt" effect gives rise to a shift in color and a diminution in the speed of the reaction corresponding exactly with the results produced by an increasing concentration of the H^+ ion.

6. Within certain limited ranges the speed of the reaction may be used

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[1] Work in this direction is being carried on by Mr. L. W. Stebbings of this laboratory.

as a dynamic method for determining, with fair precision, the concentration of the H^+ ion.

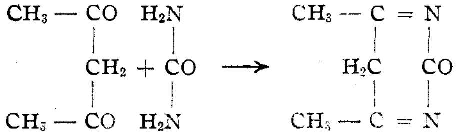
BERKELEY, CALIF.

THE CONSTITUTION OF ACETYLACETONE-UREA.

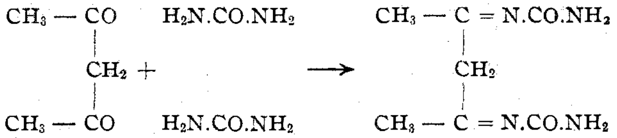
BY WILLIAM J. HALE.

Received October 16, 1913.

As first reported by Evans[1] and shortly afterwards by A. and C. Combes,[2] the condensation of acetylacetone and urea may proceed in either of two ways. The more stable product, called by Evans, acetylacetone-urea and the second, called diurimidoacetylacetone, were described at length in a second contribution.[3] The condensations were looked upon as proceeding in the following manner:



[1]

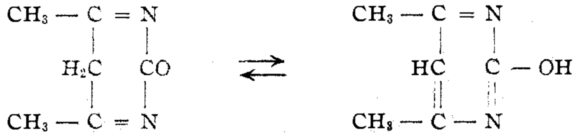


$$\begin{array}{lcl} CH_3-CO \quad H_2N.CO.NH_2 & & CH_3-C=N.CO.NH_2 \\ \quad | & & \quad | \\ CH_2 + & \longrightarrow & CH_2 \\ \quad | & & \quad | \\ CH_3-CO \quad H_2N.CO.NH_2 & & CH_3-C=N.CO.NH_2 \end{array}$$

[4]

The ease with which this acetylacetone-urea gave salts with heavy metals was thought to be due to its ready transformation into an enolic form [2]:

[1]



[2]

If this assumption were correct we should have, for consideration, a 2-hydroxypyrimidine; a compound of the type described by Hale and Brill[4] in work upon urea and a β-dialdehyde. With the exception of certain uracil derivatives,[5] which may exist in such tautomeric form, we note a marked absence of description of 2-hydroxypyrimidines in the literature. It seemed well, therefore, to undertake further investigation upon this product of Evans' in order to study the distinctive properties of 2-hydroxypyrimidines as a class.

According to Evans, the usual reactions characteristic of an hydroxyl

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[1] *J. prakt. Chem.*, [2] 46, 352 (1892).

[2] *Bull. soc. chim.*, [3] 7, 791 (1892).

[3] *J. prakt. Chem.*, [2] 48, 489 (1893).

[4] THIS JOURNAL, 34, 82 (1912).

[5] *J. prakt. Chem.*, [2] 47, 201 (1893).