Calc. for $C_6H_6OCH_3(OCOC_2H_2C_4H_5)_5$: C, 74.00%; H, 5.21%. Found: C, 74.13 and 74.06; H, 5.34 and 5.46.

Nitration of Pinite.—One gram of anhydrous pinite was dissolved in a mixture of 5 cc. of fuming nitric acid and 10 cc. of sulfuric acid. The colorless oil which separated was poured into water. The white syrup which gradually formed was purified by dissolving in alcohol and pouring into water. The syrup which separated was soluble in alcohol, methyl alcohol, ethyl and amyl acetates, acetone, ether, benzene, pyridine, chloroform, carbon disulfide and in glacial acetic acid, but did not crystallize. It was insoluble in ligroin and in water. It possessed a bitter taste, easily decomposed on heating, and exploded when struck with a hammer.

Action of Acetyl Bromide on Pinite.—By the action of acetyl bromide on pinite in a sealed tube, dibromo esters of inosite were obtained. This shows that the methoxy group was also effected by the acid bromide.

Five grams of pinite (dried at 110°) and 19 g. of acetyl bromide were placed in a sealed tube. After remaining 72 hours at room temperature, a dark red solution resulted. This was emptied into water and an oil separated which gradually solidified. The mass was filtered, dissolved in hot alcohol, and on cooling separated as a fine, crystalline substance. This proved to be a mixture, which was separated by fractional crystallization from alcohol. Scaly crystals of α-dibromotetracetylcylcohexantetrol and large prisms of β-dibromotetracetylcyclohexantetrol were obtained. The water solution obtained above was evaporated to 50 cc. and combined with the alcoholic mother liquors and the mixture boiled with animal charcoal for five hours. The resulting pale yellow solution was concentrated to 25 cc. and set away in the ice box over calcium chloride for several days. Colorless, prismatic crystals of dibromocyclohexantetrol, m. p. 216°, were obtained.

On analysis, α-dibromotetracetylcyclohexantetrol gave Br = 33.80%; calc. for $C_6H_6Br_2(OCOCH_3)_4$: 33.75%.

β-Bromotetracetyl glucose containing a trace of impurity readily decomposes. This was noticeable in the case of the halide esters of inosite but to a lesser extent.

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TEMPERATURE COEFFICIENTS AND THE EFFECTS OF ACIDS, BASES AND SALTS IN REACTION VELOCITIES OF THE TRIPHENYLMETHANE DYES.

BY H. C. BIDDLE AND C. W. PORTER.

1. Introduction.

The study of color changes among acid and basic derivatives of triphenylmethane has engaged the attention of many investigators.

As early as 1888 Nietzki[1] attributed a quinoid structure to the colored

[1] *Organische Farbstoffe*, 1888.

forms of triphenylmethane dyes. In 1892 Bernthsen[1] produced evidence that phenolphthalein derivatives have the lactone structure in their colorless forms and the quinoid arrangement in the colored modifications. K. H. Meyer and A. Hantzsch[2] have prepared double salts of quinoidal phenolphthalein with aluminum chloride and with stannic chloride. They studied the colors and absorption spectra of these components and in their opinion the colored form is invariably quinoidal. It is unnecessary to review the vast amount of work that has been done in establishing the nature of the dynamic isomerism of triphenylmethane derivatives. The fact that it consists of an establishment of equilibrium between benzoid and quinoid forms is generally recognized. The evidence upon which this conclusion is based has been critically examined by Stieglitz[3] in his "Theory of Indicators;" and a summary of the early researches in this field is included in Ley's "Farbe und Konstitution bei Organischen Verbindungen."[4] An interpretation of tautomeric change based on the movement of an electron from one part of the molecule to another[5] has also been suggested, in connection with an oscillatory shift in constitution, as a possible explanation of color in the case of the triphenylmethane dyes.[6]

Several investigators have studied the velocity of changes among dyes of the triphenylmethane series and related bodies. Hantzsch[7] and others employed the variation in electrical conductance as a measure of the speed. Sidgwick[8] and his co-workers used a colorimetric method in determining the speed of change in diamino derivatives of triphenylcarbinol in the presence of acids and bases. Biddle[9] employed a similar method in studying the conversion of triamino derivatives from the colorless into the colored forms under the influence of varying concentrations of hydrogen ion. He also noted the influence of neutral salts upon the reaction and made a preliminary study of this effect. This was followed by a study of the rate of fading of crystal violet in acid solution by Adams and Rosenstein.[10]

As pointed out by Biddle,[11] the effect of varying the concentration of hydrogen ion upon crystal violet and related bodies is two-fold. One effect is instantaneous producing in the colored form a change of tint.

[1] *Chem. Ztg.*, **16**, 1957 (1892).

[2] *Ber.*, **40**, 3497 (1907).

[3] THIS JOURNAL, **25**, 1112 (1903).

[4] Leipzig, 1911.

[5] See Lewis, THIS JOURNAL, **35**, 1448 (1913).

[6] Adams and Rosenstein, *Ibid.*, **36**, 1452 (1914).
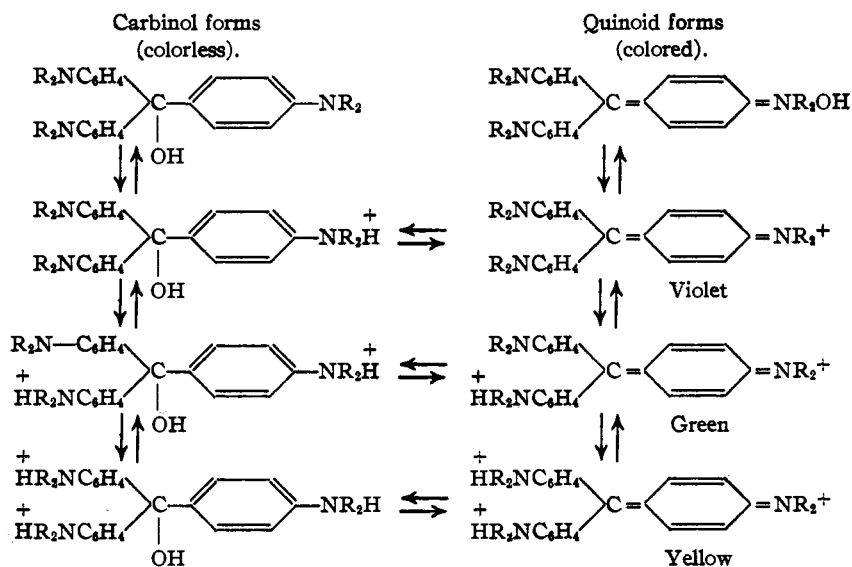
[7] Hantzsch and Kolb, *Ber.*, **32**, 3109 (1899).

[8] Sidgwick and Moore, *Z. physik. Chem.*, **58**, 385 (1907) and *J. Chem. Soc.*, **95**, 889 (1909); Sidgwick and Rivett, *Ibid.*, **95**, 899 (1909).

[9] THIS JOURNAL. **35**, 273 (1913); **36**, 84 (1914).

[10] *Ibid.*, **36**, 1454 (1914).

[11] *Ibid.*, **36**, 85 (1914).

The other is a time reaction leading to an alteration in the intensity of the color. It was further indicated that any equilibrium between benzoid and quinoid forms involves equilibria between the mono-, di-, and tri-basic ions of the colored and colorless forms. This idea has been elaborated by Adams and Rosenstein[1] who, following the suggestions of Rosenstiehl,[2] assume the formation of a series of intermediate benzoid ions of the type $(R_2N-C_6H_4)_3C$. Since, as indicated by E. and O. Fischer,[3] the conversion of carbinol ion to quinoid ion may take place directly by loss of water, it is simpler to represent the equilibrium as existing solely between these two types. The forms between which equilibrium obtains in a solution of crystal violet we would, consequently, express as follows:[4]

Carbinol forms (colorless). Quinoid forms (colored).

$R_2NC_6H_4$ — C — NR_2 — OH

$R_2NC_6H_4$ >C= $=NR_2OH$

$R_2NC_6H_4$ — C — NR_2H^+ ⇄ $R_2NC_6H_4$ >C= $=NR_2^+$ Violet

$R_2N-C_6H_4$ / $HR_2NC_6H_4^+$ — C — NR_2H^+ ⇄ $R_2NC_6H_4$ / $HR_2NC_6H_4^+$ >C= $=NR_2^+$ Green

$HR_2NC_6H_4^+$ / $HR_2NC_6H_4^+$ — C — NR_2H^+ ⇄ $HR_2NC_6H_4^+$ / $HR_2NC_6H_4^+$ >C= $=NR_2^+$ Yellow

Changes produced by varying the concentration of the H^+ ion produce instantaneous alteration in the ionic condition of the colored or colorless forms, as represented by the shifts in a vertical direction. In the quinoid forms, this is shown by an instantaneous change in tint. Simultaneously there begins an alteration in intensity of tint as quinoid or carbinol form shifts, ordinarily at a measurable speed, towards a condition of equilibrium. This is represented by the constitutional changes in the hori-

[1] THIS JOURNAL, 36, 99 (1914).

[2] Bull. soc. chim., [2] 33, 342 (1880); Compt. rend., 116, 194 (1891); Ibid., 120, 192, 264, 331, 740 (1895).

[3] Ber., 12, 2348 (1879). Compare also E. Fischer and Jennings, Ber., 26, 2222 (1893).

[4] Since a rosaniline dye is capable of adding four mols of hydrogen chloride, an additional form would seem necessary, but this would be equivalent in type to the completely ionized carbinol and may consequently be omitted.

zontal direction, which take place with the loss or addition of a molecule of water.

The present investigation was undertaken: first to ascertain the influence of changes of temperature upon the velocity of the development of color and the rate of fading of the triphenylmethane dyes; secondly, to determine to a fuller extent the effect of varying the concentration of acid and base in producing these changes; and, thirdly, to extend the work of Biddle on the neutral salt effect.

2. General Method of Procedure.

The speed of the reaction was determined in every case by following the rate of fading or of the development of color in a Stammer colorimeter. A solution of crystal violet hydrochloride was prepared in 40% alcohol containing 1 g. of dye salt per liter. Fifty cubic centimeters of this solution were diluted to one liter in 40% alcohol for a stock solution. It contained, therefore, 5×10^{-5} g. of the dye per cubic centimeter. Two cubic centimeters of the stock solution were mixed with 10 cc. of potassium hydroxide solution in each fading experiment, so that the final concentration of the dye was 8.33×10^{-6} g. per cc. The standard color for comparison was made by diluting 10 cc. of the stock solution with 50 cc. of distilled water.

In the measurements of the rate of acquiring color, a stock solution of exactly the same concentration was prepared; but before diluting to the required volume 20 cc. of normal potassium hydroxide were added to convert the dye salt into the colorless carbinol. Two cubic centimeters of this solution were mixed with 10 cc. of acid in each color development experiment. The standard for color comparison was made by adding 10 cc. of the carbinol solution to 50 cc. of acid of known concentration and the mixture was allowed to stand in a thermostat at constant temperature two hours before using.

In order to determine the velocity constant with a fair degree of precision, an air thermostat was constructed in which the colorimeter and solutions could be held at any required temperature. The thermoregulator was sufficiently sensitive to insure a temperature constant within $0.2°$. The apparatus consisted of an asbestos lined box provided with glass windows through which the thermometers, regulator, fan and colorimeter scale could be observed. Two arm holes were provided to allow the operator to mix the solutions and place them in tubes in the instrument without removing them from the air bath. When not in use the arm holes were covered with felt pads.

The source of heat was a bank of electric lights connected to the light circuit through a relay which was connected in turn with a mercury-toluene thermoregulator. The air in the apparatus was kept in rapid circulation by means of an electric fan. The standard color solutions

stood in flasks on shelves in the air bath two hours before using, this time being required to insure equilibrium in the reaction. A much shorter time would suffice to bring the solutions to the constant temperature of the air bath. The reaction mixture for comparison with the standard color was prepared as follows: Two cc. of the carbinol solution (or dye) were run from a long-stemmed buret into one arm of a branched tube, Fig. 1. Ten cc. of acid (or base) were then delivered from a buret into the other branch of the tube. The tube was stoppered and placed in the thermostat, care being exercised to avoid mixing the two solutions. From six to ten of these tubes were prepared for each concentration of acid or base used at each temperature, so that the results tabulated below are average results of six or more separate determinations in each case. The exact time of mixing the solutions in the branched tubes was determined by means of a stop watch provided with a mercury contact for the second hand and connected with a battery and an electric bell. One-minute intervals were thus announced by the ringing of the bell.
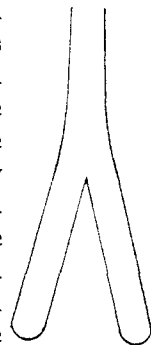

Fig. 1.

The branched tube was vigorously shaken without removing it from the thermostat and its contents were transferred to a 50 mm. tube and inserted in the colorimeter. Readings were taken at two-, three-, or four-minute intervals, the bell relieving the operator of the necessity of simultaneously watching the clock and matching the colors.

The amount of carbinol changed in a given time is proportional to the length of column of standard solution required to match the color produced, and therefore the length of column may be substituted for the concentration of the colored form. The reaction is monomolecular with respect to the dye and the velocity constants were calculated from the equations $K_1 = 1/t \log a/a - x$ and $K_2 = 1/t_2 - t_1 \log a - x_1/a - x_2$. If x is the length in mm. of the column of standard color solution required at any time to match the color produced in a 50 mm. tube, then the value $(a - x)$ is obtained by subtracting from fifty the reading in millimeters on the colorimeter scale. In the fading experiments the colorimeter reading gives directly the value of $(a - x)$ since the reading approaches zero as the reaction approaches equilibrium.

3. Temperature Coefficient (Colorless to Colored).

The following tables give the velocity constants for crystal violet at four temperatures with varying concentrations of acid. The normality of the acid given in connection with each table refers to the free hydrochloric acid present in the solution after mixing the components and deducting the amount of acid neutralized by the excess of potassium hydroxide in the carbinol solution.[1]

[1] A slight excess of base is necessary to hold the dye in the colorless form but the excess is easily estimated by titration. See Biddle, THIS JOURNAL, 36, 84 (1914).

CRYSTAL VIOLET, TABLES I TO XIX.

TABLE I.—TEMP. 25°. 0.0026·N HCl.			
Time. Min.	Reading (X).	K_1.	K_2.
2	18.5	0.1010	0.1010
4	30.0	0.0995	0.0979
6	37.4	0.0998	0.1003
8	42.1	0.1001	0.1013
10	45.0	0.1000	0.0993
	Mean,	0.1001	0.1000

TABLE II.—TEMP. 30°. 0.0026 N HCl.			
Time. Min.	Reading (X).	K_1.	K_2.
2	27.2	0.1705	0.1705
4	40.0	0.1747	0.1789
6	44.9	0.1652	0.1462
8	47.6	0.1648	0.1637
	Mean,	0.1688	0.1648

TABLE III.—TEMP. 35°. 0.0026 N HCl.			
2	36.0	0.2764	0.2764
3	42.5	0.2746	0.2711
4	46.0	0.2742	0.2730
	Mean,	0.2751	0.2735

TABLE IV.—TEMP. 25°. 0.0051 N HCl.			
4	10.5	0.0255	0.0255
8	18.8	0.0256	0.0256
12	24.8	0.0247	0.0231
16	29.9	0.0247	0.0245
20	33.6	0.0242	0.0220
	Mean,	0.0249	0.0242

TABLE V.—TEMP. 30°. 0.0051 N HCl.			
6	22.0	0.0419	0.0419
8	26.9	0.0419	0.0417
10	31.0	0.0420	0.0424
12	34.3	0.0419	0.0414
14	36.6	0.0408	0.0344
	Mean,	0.0412	0.0403

TABLE VI.—TEMP. 35°. 0.0051 N HCl.			
4	25.0	0.0750	0.0750
6	32.2	0.0745	0.0737
8	36.7	0.0717	0.0632
10	40.2	0.0706	0.0663
12	43.0	0.0710	0.0730
	Mean,	0.0726	0.0703

TABLE VII.—TEMP. 40°. 0.0051 N HCl.			
4	34.1	0.1243	0.1243
6	40.5	0.1201	0.1118
8	44.5	0.1198	0.1186
10	46.8	0.1193	0.1176
	Mean,	0.1209	0.1181

TABLE VIII.—TEMP. 25°. 0.0068 N HCl.			
4	6.9	0.0161	0.0161
8	12.7	0.0159	0.0156
12	17.9	0.0160	0.0163
16	22.3	0.0160	0.0160
20	26.1	0.0160	0.0160
	Mean,	0.0160	0.0160

TABLE IX.—TEMP. 30°. 0.0068 N HCl.			
4	11.6	0.0286	0.0286
8	19.7	0.0271	0.0257
12	24.7	0.0246	0.0195
16	30.4	0.0254	0.0277
20	33.9	0.0246	0.0213
	Mean,	0.0261	0.0246

TABLE X.—TEMP. 35°. 0.0068 N HCl.			
4	17.1	0.0454	0.0454
8	27.6	0.0435	0.0417
12	35.2	0.0440	0.0449
16	40.1	0.0439	0.0436
20	43.2	0.0433	0.0407
	Mean,	0.0440	0.0439

TABLE XI.—TEMP. 40°. 0.0068 N HCl.   TABLE XII.—TEMP. 25°. 0.0151 N HCl.

Time Min.	Reading (X).	K_1.	K_2.	Time Min.	Reading (X).	K_1.	K_2.
4	24.5	0.0731	0.0731	4	4.4	0.0100	0.0100
6	31.7	0.0727	0.0720	12	12.0	0.0099	0.0099
8	37.0	0.0731	0.0742	20	18.0	0.0096	0.0093
10	40.7	0.0730	0.0722	28	22.9	0.0095	0.0090
12	43.4	0.0732	0.0744	36	27.2	0.0094	0.0093
	Mean,	0.0730	0.0732		Mean,	0.0096	0.0095

TABLE XIII.—TEMP. 30°. 0.0151 N HCl.   TABLE XIV.—TEMP. 35°. 0.0151 N HCl.

4	6.6	0.0153	0.0153	8	18.5	0.0251	0.0251
8	12.3	0.0153	0.0152	12	25.1	0.0252	0.0255
12	17.2	0.0152	0.0151	16	30.2	0.0251	0.0248
16	21.5	0.0152	0.0152	20	34.0	0.0246	0.0228
20	25.3	0.0153	0.0155	24	37.1	0.0244	0.0233
	Mean,	0.0153	0.0153		Mean,	0.0255	0.0243

TABLE XV.—TEMP. 40°. 0.0151 N HCl.   TABLE XVI.—TEMP. 25°. 0.0234 N HCl.

8	27.3	0.0428	0.0428	4	4.0	0.0090	0.0090
10	31.3	0.0426	0.0421	12	11.0	0.0089	0.0089
12	34.6	0.0426	0.0421	20	17.3	0.0092	0.0095
14	37.5	0.0429	0.0453	28	22.0	0.0089	0.0084
16	39.6	0.0432	0.0449	36	26.1	0.0088	0.0085
	Mean,	0.0430	0.0434		Mean,	0.0090	0.0089

TABLE XVII.—TEMP. 30°. 0.0234 N HCl.   TABLE XVIII.—TEMP. 35°. 0.0234 N HCl.

8	12.1	0.0150	0.0150	8	18.1	0.0243	0.0243
16	21.2	0.0149	0.0149	12	24.6	0.0245	0.0247
24	28.3	0.0150	0.0153	16	29.7	0.0246	0.0243
32	33.5	0.0149	0.0148	20	33.7	0.0243	0.0238
36	35.6	0.0149	0.0147	24	36.7	0.0239	0.0221
	Mean,	0.0150	0.0149		Mean,	0.0243	0.0238

TABLE XIX.—TEMP. 40°. 0.0234 N HCl.

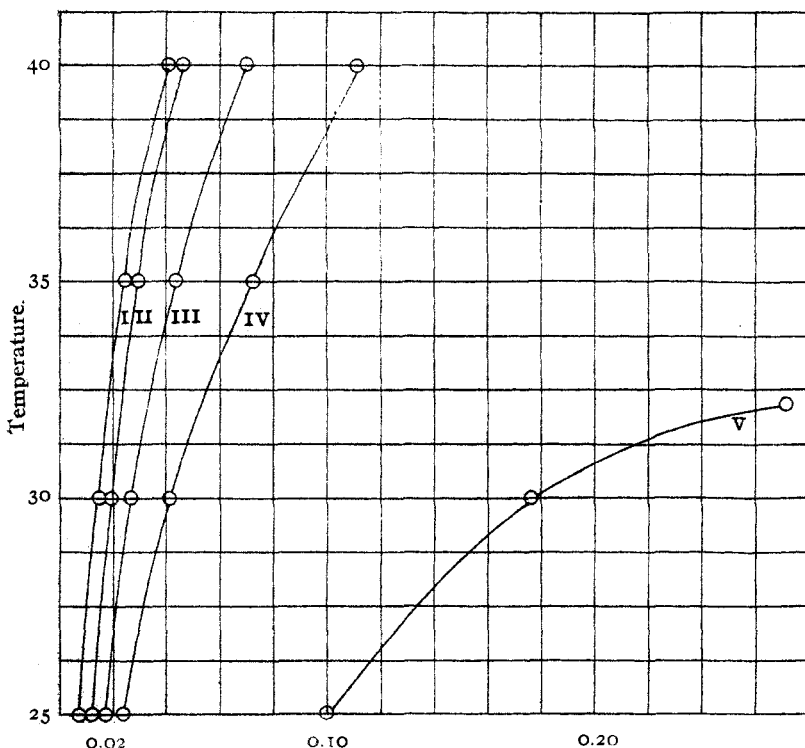| Time. Min.	Reading (X).	K_1.	K_2.
8	26.1	0.0400	0.0400
10	30.1	0.0400	0.0397
12	33.5	0.0400	0.0406
14	36.2	0.0399	0.0388
16	38.5	0.0398	0.0395
	Mean, 0.0399	Mean,	0.0397

Fig. 2.

$K \times 10^2$.

These results are plotted in Fig. 2. The velocity constants multiplied by 100 are represented as abscissae and temperature as ordinates. The curves refer to crystal violet in various concentrations of hydrochloric acid as follows:

Curve I, 0.0234 N HCl; II, 0.0151 N HCl; III, 0.0068 N HCl; IV, 0.0051 N HCl; V, 0.0026 N HCl.

Within the range of these experiments the temperature coefficient appears to be independent of the concentration of the acid employed. A rise of five degrees increases the velocity 66%. We may, therefore, express the relationship between the velocities at temperatures t_1 and t_2 by the empirical formula

$$K_{t_2} = K_{t_1}(1.1066)^{t_2 - t_1}$$

or employing the more general formula proposed by Arrhenius,

$$\log \frac{K_{t_2}}{K_{t_1}} = A(t_2 - t_1),$$

the value of the constant A is found to be 0.044.

This equation enables us to calculate the error in the above results, due to the heat of solution of 2 cc. of 40% alcohol in 10 cc. of dilute acid. The rise in temperature varies slightly with the concentration of the acid and temperature of the components before mixing. The maximum eleva-

tion of temperature in the above experiments reached $0.6°$. The rate of cooling was such that in every instance the temperature of the mixture in the color comparison tube was within $0.4°$ of the temperature of the air bath at the end of four minutes. The exact temperature of the air bath was attained in from twelve to fifteen minutes.

Rejecting the readings taken during the first four minutes and applying the above formula in the calculation of the error we find that the maximum deviation of temperature introduces variation in the third decimal place of the velocity constant. It is evident then that in the experiments that were completed within fifteen minutes the constants reported have no real significance beyond the third decimal place. In very rapid reactions the readings made within the first four minutes have been retained, but the results in these cases cannot be exact.

Table XX gives the ratios between the velocity constants (K_1) at different temperatures for various concentrations of hydrochloric acid. The ratio is quite constant for any five-degree interval, being apparently independent of the temperature and also independent of the concentration of the acid.

TABLE XX.

Concentration of acid.	$\dfrac{K_1{}^{30°}}{K_1{}^{25°}}$	$\dfrac{K_1{}^{35°}}{K_1{}^{30°}}$	$\dfrac{K_1{}^{40°}}{K_1{}^{35°}}$
$0.0026\ N$	1.68	1.63	*
$0.0051\ N$	1.68	1.73	1.67
$0.0068\ N$	1.61	1.68	1.66
$0.0151\ N$	1.58	1.67	1.68
$0.0234\ N$	1.67	1.63	1.65

Average ratio, 1.66.

* With $0.0026\ N$ acid at $40°$ the reaction ran to completion within two minutes.

4. Temperature Coefficient (Colored to Colorless).

In the fading reaction the temperature coefficient is smaller than in the reverse change. It is independent of the concentration of the base and has the same value for all temperatures between $25°$ and $40°$ as indicated in Tables XXI to XXXII.

In each case the concentration of the dye was 8.33×10^{-6} g. per cubic centimeter.

CRYSTAL VIOLET, TABLES XXI—XXXII.

TABLE XXI.—TEMP. $25°$. $0.0033\ N$ KOH.

Time.	Reading $(a-x)$.	K_1.	K_2.
12	29.6	0.0189	0.0189
15	25.9	0.0190	0.0193
18	22.8	0.0189	0.0184
21	20.0	0.0189	0.0189
24	17.5	0.0190	0.0193
		Mean, 0.0189	0.0190

TABLE XXII.—TEMP. $30°$. $0.0033\ N$ KOH.

Time.	Reading $(a-x)$.	K_1.	K_2.
12	24.7	0.0255	0.0255
16	18.5	0.0263	0.0313
20	14.3	0.0266	0.0279
24	11.2	0.0266	0.0265
28	8.8	0.0265	0.0261
		Mean, 0.0263	0.0274

TABLE XXIII.—TEMP. 35°.   0.0033 N KOH.

Time.	Reading $(a-x)$.	K_1.	K_1.
12	17.6	0.0378	0.0378
16	12.6	0.0374	0.0363
20	8.7	0.0379	0.0402
24	6.2	0.0377	0.0367
28	4.4	0.0377	0.0372
	Mean,	0.0377	0.0377

TABLE XXIV.—TEMP. 40°.   0.0033 N KOH.

Time.	Reading $(a-x)$.	K_1.	K_2.
10	14.6	0.0534	0.0534
12	11.4	0.0534	0.0537
14	8.9	0.0535	0.0537
16	6.9	0.0537	0.0552
18	5.4	0.0536	0.0532
	Mean,	0.0535	0.0538

TABLE XXV.—TEMP. 25°.   0.0050 N KOH.

9	27.4	0.0290	0.0290
12	22.4	0.0290	0.0291
15	18.4	0.0289	0.0284
18	15.0	0.0290	0.0295
21	12.3	0.0289	0.0286
	Mean,	0.0290	0.0289

TABLE XXVI.—TEMP. 30°.   0.0050 N KOH.

6	28.8	0.0399	0.0399
9	22.0	0.0396	0.0389
12	16.6	0.0399	0.0407
15	12.5	0.0401	0.0410
18	9.5	0.0400	0.0397
	Mean,	0.0399	0.0400

TABLE XXVII.—TEMP. 35°.   0.0050 N KOH.

6	22.5	0.0578	0.0578
8	17.5	0.0569	0.0545
10	13.5	0.0568	0.0563
12	10.4	0.0568	0.0566
14	8.0	0.0568	0.0569
	Mean,	0.0570	0.0564

TABLE XXVIII.—TEMP. 40°.   0.0050 N KOH.

8	10.7	0.0837	0.0837
10	7.4	0.0829	0.0801
12	5.1	0.0826	0.0808
14	3.5	0.0825	0.0817
16	2.4	0.0824	0.0819
	Mean,	0.0828	0.0816

TABLE XXIX.—TEMP. 25°.   0.0083 N KOH.

6	25.7	0.0481	0.0481
9	18.3	0.0485	0.0468
12	12.9	0.0409	0.0506
15	8.8	0.0502	0.0553
18	6.3	0.0494	0.0483
	Mean,	0.0474	0.0498

TABLE XXX.—TEMP. 30°.   0.0083 N KOH.

6	20.0	0.0663	0.0663
9	12.7	0.0662	0.0660
12	8.2	0.0655	0.0633
15	5.5	0.0639	0.0578
18	3.5	0.0639	0.0637
	Mean,	0.0651	0.0634

TABLE XXXI.—TEMP. 35°.   0.0083 N KOH.

4	21.1	0.0936	0.0936
6	13.7	0.0937	0.0937
8	9.0	0.0930	0.0912
10	5.9	0.0928	0.0916
12	3.9	0.0923	0.0898
	Mean,	0.0931	0.0920

TABLE XXXII.—TEMP. 40°.   0.0083 N KOH.

4	14.5	0.1344	0.1344
6	7.8	0.1344	0.1346
8	4.3	0.1331	0.1293
10	2.4	0.1318	0.1266
	Mean,	0.1334	0.1312

The ratio between the velocity constants at four temperatures with varying concentrations of potassium hydroxide are given in Table XXXIII.

TABLE XXXIII.

Concentration of base.	$\dfrac{K_1{}^{30°}}{K_1{}^{25°}}$	$\dfrac{K_1{}^{35°}}{K_1{}^{30°}}$	$\dfrac{K_1{}^{40°}}{K_1{}^{35°}}$
0.0033 N	1.40	1.44	1.44
0.0050 N	1.38	1.43	1.48
0.0083 N	1.38	1.42	1.43

Average ratio, 1.43.

Employing the formula $\log K_{t_2}/K_{t_1} = A(t_2 - t_1)$ we may calculate with fair precision the constant at any temperature if the constant at any other temperature is known. In this case $A = 0.03107$. Or we may employ the equation $K_{t_2} = K_{t_1}(1.074)^{t_2-t_1}$. The acceleration per five degrees is 43%. Since the temperature effect per degree is smaller than in the acid reactions the error due to the heat of solution of the alcohol is also smaller.

The velocity constants for the fading reactions are plotted as abscissae and the concentration of alkali as ordinates in Fig. 3.
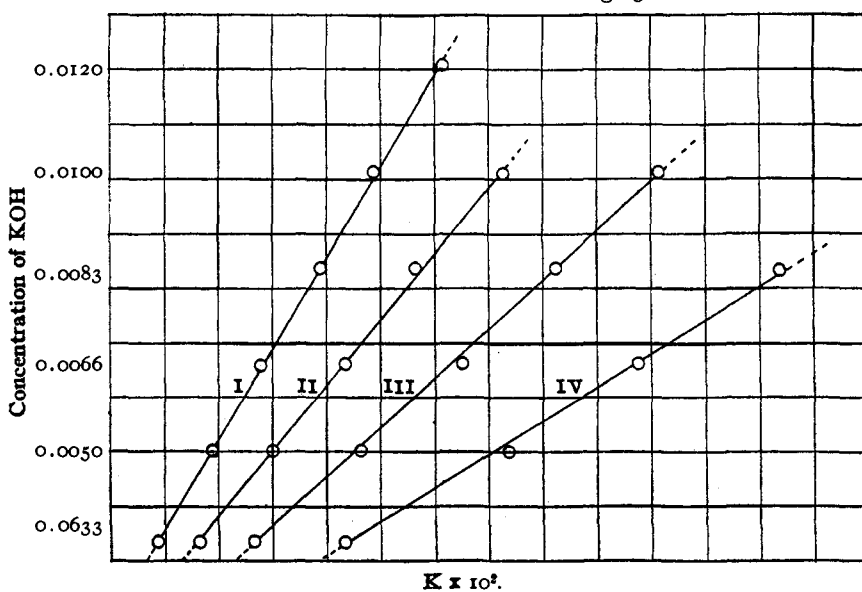

K x 10².

Fig. 3.

The curves are isothermals showing the relation of velocity of fading, concentration of alkali and temperature. Curve I is at 25°; II, 30°; III, 35°; and IV, 40°.

5. Effect of OH Ion upon the Speed of the Reaction.

The rate of fading of triphenylmethane dyes, under the influence of an alkali, increases with increasing concentration of the alkali. In the case

of basic dyes the rate is exactly proportional to the concentration of the hydroxyl ions. In the case of acid dyes, such as phenolphthalein, the increase in the velocity of fading is slightly in excess of the increase in the concentration of the hydroxyl ions. The results obtained with phenolphthalein are given in Table XXXIV.

TABLE XXXIV.—PHENOLPHTHALEIN IN ALKALINE SOLUTION AT 25°.

Normality of KOH	0.11	0.15	0.22	0.33
K_1^*	0.0280	0.0420	0.0707	0.1048
K_2^*	0.0280	0.0418	0.0715	0.1042

* Average values of many determinations. Reported in this form for economy of space.

6. Effect of H+ Ion upon the Speed of the Reaction.

Under the direction of Professor Biddle a monamino triphenylmethane was synthesized by J. N. Lahiri[1] and the observation was made that the rate of development of color is an inverse function of the concentration of the hydrogen ions. The dye was, however, so faintly basic that the salt formed was largely hydrolyzed and the intensity of the color was insufficient for accurate measurement. The speeds of the corresponding reactions with diamino derivatives were determined by Sidgwick and Moore[2] and Sidgwick and Rivett[3] who found the velocity of color development to be proportional to the two-thirds power of the acid concentration. With a triamino derivative Biddle[4] found that, within a certain range, the speed of acquiring color is inversely proportional to the square of the hydrogen ion concentration.

Extending these researches over a wider range of acid concentration, the interesting fact is disclosed that each of these basic triphenylmethane derivatives acquires color at a rate varying with the concentration of the acid in such a way that the rate passes through a minimum at a certain definite acid concentration. The possibility of this effect was pointed out by Adams and Rosenstein in the case of crystal violet.[5] The particular concentration corresponding to the minimum is different for the different dyes. That is to say, increasing the acid content of the reaction mixture, up to a certain limit, retards the speed of the reaction, but increasing the quantity of acid beyond that limit accelerates the change.

Thus for crystal violet the constants at 25° are as follows:

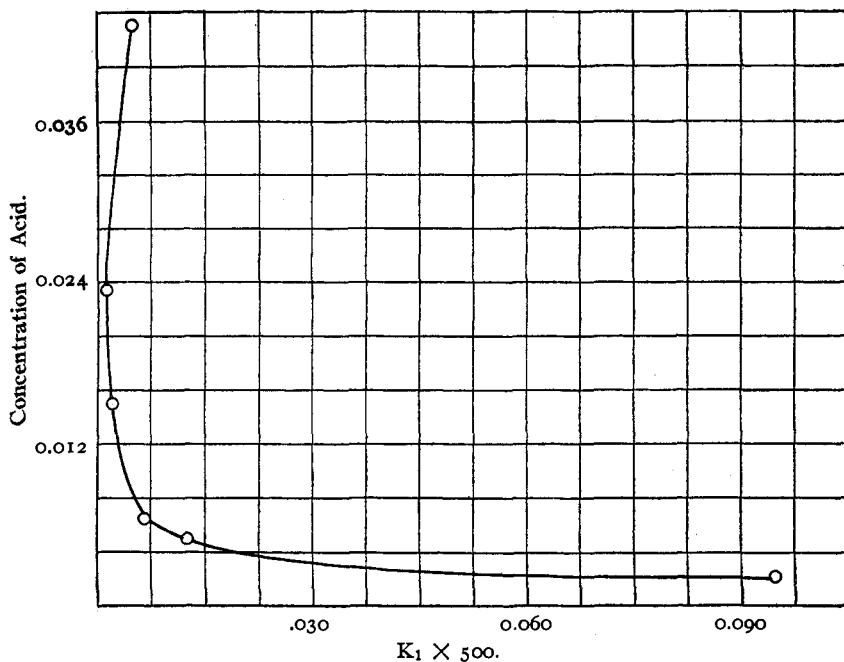| Normality of acid	0.0432	0.0234	0.0151	0.0068	0.0051	0.0026
K_1	0.01170	0.00899	0.00969	0.01628	0.02482	0.10009

This is shown graphically in Fig. 4.

[1] Unpublished Thesis, 1914,. U. of Cal.
[2] J. Chem. Soc., **95**, 889 (1909).
[3] Ibid., **95**, 899 (1909).
[4] THIS JOURNAL, **36**, 84 (1914).
[5] Ibid., **36**, 1452 (1914).

K₁ × 500.

Fig. 4.

The minimum rate corresponds to a concentration of approximately 0.0234 N hydrochloric acid. In the case of malachite green the acid concentration corresponding to the minimum rate is approximately 0.007 N. This is indicated in Table XXXV.

It must be remembered, however, that these velocity constants are measures of the rates of approach to the colors of equilibrium mixtures in each of the given acid concentrations and not measures of the absolute velocities of reaction. The values are, therefore, not strictly comparable.[1] Table XXXV shows the effect of varying the acid concentration on malachite green carbinol.

TABLE XXXV.—MALACHITE GREEN. TEMPERATURE 25°.

Normality of HCl	0.065	0.023	0.015	0.007	0.005	0.003
K_1	0.1224	0.1092	0.0645	0.0480	0.0559	0.0628
K_2	0.1227	0.1101	0.0672	0.0465	0.0553	0.0623

7. The Neutral Salt Effect.

In many types of chemical change in which acids or bases are active catalysts the velocity constants are changed by the addition of small quantities of neutral salts. This phenomenon was investigated by Arrhenius[2] in connection with the rate of hydrolysis of cane sugar. He found

[1] See Biddle, THIS JOURNAL, 36, 90 (1914).

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

that the speed of the reaction was increased to practically the same extent by equimolecular quantities of neutral salts if these salts were equally ionized. Salts having the smallest dissociation constants were least effective. He observed, moreover, that any particular salt produces a greater relative change in the presence of dilute acid than in more concentrated acid solutions. And Arrhenius attributed the salt effect to more than one cause, e. g., the direct catalyzing influence of the salt molecules, and the formation of new electrolytes in the solution. Euler[1] made a similar explanation and suggested that the ionization of the solvent may be increased by the presence of salts and the catalytic influence of the salt is largely due to this effect. Acree,[2] on the other hand, believes "that catalysis by salts or other neutral substances is due not so much to a change in the dissociation constant of the water as to a number of other factors" which he enumerates as effects of the salt upon the viscosity of the solution, the solvation of the ions and undissociated molecules, the combination of the salt with the molecules undergoing transformation, and the influence of the salt upon the thermodynamic potentials of the reacting ions or molecules.

Stieglitz[3] has expressed the opinion that the salt effect "is due to the fact that in salt solutions we are working with mixed solvents in which ionization, velocities, etc., cannot be expected to be the same as in a pure solvent."

In the results tabulated below are set forth the neutral salt effects upon reaction velocities which occur in transformations of dyes of the triphenylmethane series. Measurements have been made of the rates of change from the quinoid to the benzoid forms, and also the reverse changes, in the case of crystal violet and malachite green in the presence of varying quantities of neutral uniunivalent salts. Qualitative observations have been made of the effects of unibivalent and bibivalent salts under like conditions. Similar measurements have been carried out on the influence of neutral salts upon the fading of phenolphthalein in the presence of alkalies. The fading of the latter indicator, with and without neutral salts, has been a subject of study by Drs. E. Q. Adams and Merl Randall[4] and the effect of neutral salts upon the ionization of the indicator was investigated by Rosenstein.[5] Tables XXXVI to XLIX inc. refer to crystal violet.

Table XL shows the effect of sodium chloride. Each constant reported is the average of at least twenty readings. (Five readings at regular time intervals on each of at least four reaction mixtures.)

[1] Z. physik. Chem., 32, 348 (1900).

[2] Am. Chem. J., 41, 475 (1909).

[3] THIS JOURNAL, 34, 1687 (1912).

[4] Unpublished investigation.

[5] THIS JOURNAL, 36, 93 (1914).

TABLE XXXVI.—0.004 N HCl, 0.004 N KCl.

Time.	Reading (x).	K_1.	K_2.
12	30.2	0.0337	0.0337
14	33.2	0.0338	0.0356
16	35.5	0.0336	0.0319
18	37.6	0.0336	0.0339
20	39.5	0.0338	0.0361
	Mean,	0.0337	0.0342

TABLE XXXVII.—0.004 N HCl, 0.092 N KCl.

Time.	Reading (x).	K_1.	K_4.
12	18.0	0.0161	0.0161
15	21.6	0.0163	0.0172
18	24.6	0.0163	0.0161
21	27.5	0.0165	0.0175
24	29.9	0.0164	0.0163
	Mean,	0.0163	0.0166

TABLE XXXVIII.—0.004 N HCl, 0.183 N KCl.

Time.	Reading (x).	K_1.	K_2.
12	15.2	0.0131	0.0131
15	18.0	0.0121	0.0121
18	20.7	0.0128	0.0126
21	22.8	0.0124	0.0108
24	25.0	0.0125	0.0122
	Mean,	0.0125	0.0121

TABLE XXXIX.—0.004 N HCl, 0.362 N KCl.

Time.	Reading (x).	K_1.	K_2.
9	9.6	0.0103	0.0103
12	12.6	0.0105	0.0111
15	15.3	0.0105	0.0108
18	18.0	0.0107	0.0117
21	20.0	0.0105	0.0093
	Mean,	0.0105	0.0106

TABLE XL.—CRYSTAL VIOLET IN 0.004 N HCl WITH NaCl.

Normality of NaCl	0.004	0.092	0.183	0.362
K_1	0.0334	0.0186	0.0133	0.0105
K_2	0.0333	0.0188	0.0133	0.0102

It is evident that the rate of developing color in crystal violet becomes slower as the concentration of the salt increases and a comparison of Table XL with the results given in Tables XXXVI to XXXIX reveals the fact that equimolecular quantities of KCl and NaCl are equally effective in retarding the change. The rate of development of color is likewise retarded by the presence of salts as indicated in Tables XLI to XLIX.

CRYSTAL VIOLET IN ALKALINE SOLUTIONS.

TABLE XLI.—0.0104 N KOH. No SALT.

Time.	Reading ($a - x$).	K_1.	K_2.
10	13.0	0.0585	0.0585
12	9.9	0.0577	0.0591
14	7.6	0.0577	0.0574
16	5.8	0.0578	0.0586
18	4.4	0.0580	0.0599
	Mean,	0.0579	0.0587

TABLE XLII.—0.0104 N KOH, 0.284 N NaCl.

Time.	Reading ($a - x$).	K_1.	K_2.
10	16.9	0.0471	0.0471
12	13.7	0.0468	0.0465
14	11.0	0.0468	0.0471
16	8.8	0.0470	0.0484
18	7.1	0.0470	0.0466
	Mean,	0.0469	0.0471

TABLE XLIII.—0.0104 N KOH, 0.608 N NaCl.			
Time.	Reading $(a-x)$.	K_1.	K_2.
10	20.0	0.0397	0.0398
12	16.6	0.0399	0.0404
14	13.5	0.0406	0.0448
16	11.5	0.0399	0.0348
18	9.5	0.0400	0.0414
	Mean,	0.0400	0.0402

TABLE XLIV.—0.0104 N KOH, 1.045 N NaCl.			
Time.	Reading $(a-x)$.	K_1.	K_2.
6	31.6	0.0332	0.0332
8	27.2	0.0330	0.0325
10	23.4	0.0339	0.0326
12	20.0	0.0331	0.0327
16	14.7	0.0330	0.0327
	Mean,	0.0332	0.0327

TABLE XLV.—0.0104 N KOH, 1.562 N NaCl.			
10	26.9	0.0269	0.0269
12	24.3	0.0261	0.0220
14	21.8	0.0257	0.0235
16	18.5	0.0270	0.0256
18	16.3	0.0270	0.0274
	Mean,	0.0265	0.0262

TABLE XLVI.—0.0104 N KOH, 2.139 N NaCl.			
10	30.1	0.0220	0.0220
12	27.0	0.0223	0.0236
14	24.0	0.0227	0.0266
16	22.0	0.0222	0.0188
18	20.0	0.0221	0.0206
	Mean,	0.0226	0.0228

The following condensed tables show similar results with different salts acting in conjunction with potassium hydroxide at various concentrations:

TABLE XLVII.—CRYSTAL VIOLET IN 0.013 N KOH WITH KNO_3.

Normality of KNO_3	0.0	0.1	0.2	0.3	0.4	0.5
K_1	0.0712	0.0520	0.0411	0.0350	0.0309	0.0259
K_2	0.0715	0.0524	0.0413	0.0356	0.0305	0.0259

TABLE XLVIII.—CRYSTAL VIOLET IN 0.013 N KOH WITH KCl.

Normality of KCl	0.0	0.1	0.2	0.3	0.4	0.5
K_1	0.0712	0.0540	0.0440	0.0380	0.0328	0.0290
K_2	0.0715	0.0545	0.0440	0.0381	0.0328	0.0290

TABLE XLIX.—CRYSTAL VIOLET IN 0.062 N KOH WITH NaCl.

Normality of NaCl	0.000	0.116	0.194	0.388	0.775	0.966
K_1	0.3592	0.2812	0.2212	0.1840	0.1442	0.1373
K_2	0.3610	0.2796	0.2191	0.1796	0.1469	0.1408

The rate of fading is approximately a linear function of the square root of the equivalent concentration of the salt as shown in Fig. 5.

The following tables, L and LI, show the salt effect on the rate of fading of phenolphthalein in different concentrations of alkali and salt. It will be observed that the salt effect is exactly opposite to that produced by salts in crystal violet. In other words, the rate of fading of phenolphthalein is accelerated by salts:

TABLE L.—PHENOLPHTHALEIN IN 0.31 N KOH WITH NaCl.

Normality of NaCl	0.000	0.116	0.194	0.388	0.966	1.940
K_1	0.1048	0.1204	0.1360	0.1451	0.1555	0.1625
K_2	0.1041	0.1213	0.1357	0.1439	0.1518	0.1627

TABLE LI.—PHENOLPHTHALEIN IN 0.11 N KOH WITH NaCl.

Normality of NaCl	0.14	0.28	0.42
K_1	0.0323	0.0358	0.0419
K_2	0.0315	a.0361	0.0419

In this study, as indicated by the tables, we find that neutral salts in the presence of basic dyes behave like acids. That is to say, the addition of a quantity of a neutral salt to a solution of an acid dye, such as phenolphthalein, when fading under the influence of an alkali, produces
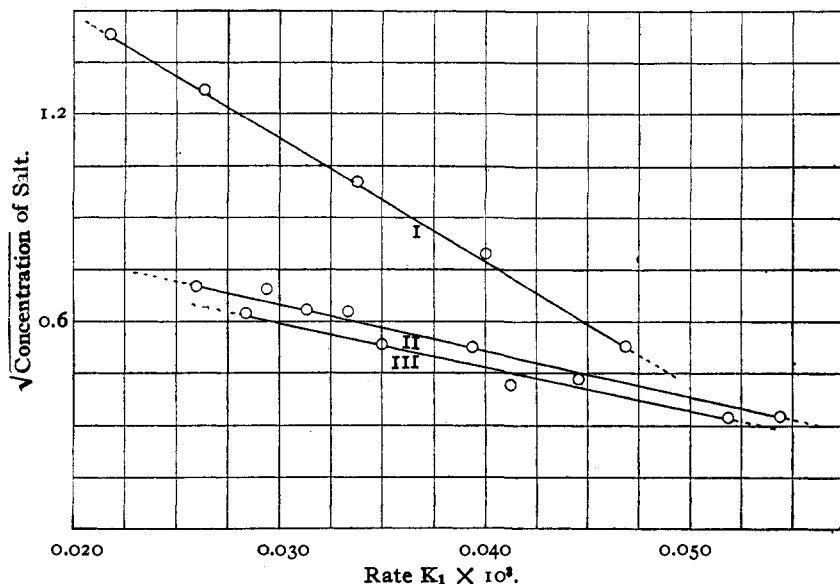

Rate $K_1 \times 10^3$.

Fig. 5.

Square roots of salt concentrations are plotted as ordinates and rates of fading as abscissae. Curve I summarizes Tables XLII to XLVI (inc.); Curves II and III represent the values reported in Tables XLVIII and XLVII, respectively.

an acceleration equivalent to that effected by increasing the concentration of the alkali; while a similar addition of salt to a basic dye such as crystal violet or malachite green when shifting under the influence of either acid or base towards a state of equilibrium produces an effect equivalent to that resulting from the addition of an acid. This means that the speed of fading of a basic dye in the presence of an alkali will in all cases be diminished by the addition of a neutral salt. In the conversion of such a dye from the carbinol to the colored form in the presence of an acid, the salt effect will be determined by the concentration of the acid and may be accelerating, retarding, or indifferent. It will be recalled that for each carbinol base there is a particular concentration of acid at which the color is developed at a minimum rate. In acids of this particular concentration, neutral salts are without effect. In solutions of higher acid con-

centration, they are found to accelerate the development of color, and in less concentrated solutions with respect to the acid, they retard the rate of assumption of color.

Misses Alice Morse and Lulu E. Vance[1] found the catalyzing effect of such uniunivalent neutral salts as sodium chloride, potassium chloride, sodium nitrate, sodium bromide, sodium iodide and potassium nitrate, to be the same in equimolecular quantities within the limits of experimental error. The results recorded in Tables XLVIII to LVIII confirm this conclusion in the case of the salts studied. Unibivalent salts of bibivalent salts, however, give variable results. This, as previously shown,[2] is to be accounted for in these cases by the variation of hydrogen ion produced by partial hydrolysis. From an inspection of Tables XXXIV to XLI it will be noted, further, that the salt effect is greatest in solutions most dilute with respect to the acid. The effect, as will be seen, decreases with increasing concentration of the acid until the acid concentration producing the minimum rate is reached. Thereafter, the effect of the salt, though slight, increases with increasing concentration. In the fading experiments it will also be noted that the salt effect is greatest in solutions of greatest dilution with respect to the alkali.

Not only is the rate of change altered by neutral salts, the equilibrium is itself displaced, as was previously pointed out by Biddle.[3] This is evident from the fact that in acid solutions, the colors produced vary with the amount of salt added, the direction of the variation being the same as that produced by increasing concentration of acid.

There is apparently no simple mathematical relation between the quantity of salt employed and the changes in velocity for the conversion of benzoid to quinoid form in the presence of acids. In the conversion of colored to colorless form, in the presence of alkalies, however, a fairly regular decrease in rate is produced by increasing concentration of salt. The rate of fading is almost a linear function of the square root of the equivalent concentration of the salt (Fig. 5). In the presence of a concentration of base exceeding $0.02\ N$, however, there is considerable deviation from this rule. In such cases the graph obtained by plotting the speed against the square root of the sum of the concentrations of salt and alkali, more closely approximates a straight line.

Alcohol and acetone accelerate the rate of fading of crystal violet, brilliant green and other basic derivatives of triphenylmethane. They also accelerate the development of color. The effect is therefore just opposite to that produced by salts. The change in rate is relatively

[1] Unpublished Thesis carried out under the direction of H. C. Biddle, Univ. of California, 1914.

[2] Biddle, This Journal. **36**, 98 (1914).

[3] *Ibid..* **36**, 86, 96 (1914).

greater as the concentration of the alcohol or acetone increases, in this respect also differing from the behavior of neutral salts. The addition of sugar reduces the rate of fading, but this is probably due to a diminution of the hydroxyl ions caused by combination of the base with the sugar molecules to form glucosates. It is possible practically to stop the progress of the fading reaction by the addition of sufficient sugar.

Summary.

1. The temperature coefficient for the conversion of a triphenylmethane carbinol into the quinoid form, in the presence of an acid, is independent of the concentration of the acid and between 25° and 40° independent also of the temperature. For crystal violet the increase in the velocity of the change is 66% for every five degrees. Changes of the same order of magnitude were observed in the case of diamino derivatives but comparatively few measurements were made with these dyes and the results have not been tabulated in this paper.

2. The temperature coefficient for the fading of a triphenylmethane dye in the presence of an alkali is independent of the concentration of the base and independent of the temperature (between 25–40°). For crystal violet the increase in velocity is 43% for five degrees.

3. For all concentrations of acid below 0.024 N the speed of the color development in crystal violet is an inverse function of the concentration of the hydrogen ions. For all concentrations of acid above this value the velocity is a direct function of the hydrogen ion concentration.

4. The rate of fading of a triphenylmethane dye is a direct function of the concentration of the hydroxyl ions and in the case of basic dyes, such as crystal violet, is exactly proportional to such concentration.

5. Neutral salts retard the rate of fading and also retard the rate of development of color in all the basic triphenylmethane dyes but accelerate the rate of fading of acidic dyes.

6. All uniunivalent neutral salts in equivalent concentrations are equally effective in modifying the catalytic influence of the acid or base. They behave like acids in their effect upon basic dyes and like bases in their influence upon acid dyes.

BERKELEY. CAL.

CONVERSION OF GALACTOSE PENTACETATE TO AN ISOMERIC FORM.

By C. S. HUDSON AND H. O. PARKER.[1]

Crystalline galactose pentacetate was prepared by Erwig and Koenigs[2]

[1] Contribution from the Carbohydrate Laboratory, Bureau of Chemistry, United States Department of Agriculture, and the Chemical Laboratory of Princeton University.

[2] Ber., 22, 2207 (1889).