

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

## Kinetics and Equilibria of the Carbinol Formation of Phenolphthalein

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## Introduction

That phenolphthalein fades in concentrated alkali was first observed by A. von Baeyer.<sup>1</sup> The rate of fading and the position of equilibrium were investigated colorimetrically by Kober and Marshall.<sup>2</sup> They attributed the fading process to the reaction of equimolecular proportions of alkali and the red form to yield a tribasic salt of phenolphthalic acid and formulated the process as



$R^-$  is the colored form,  $k_1$  is the molar rate constant for the formation of the carbinol  $ROH^{2-}$ , and  $k_2$  is the corresponding constant for the reverse reaction. Biddle and Porter<sup>3</sup> observed that the molar rate constant,  $k_1$ , increased with increasing concentration of alkali but did not account for this behavior. Thiel and Jungfer<sup>4</sup> concluded from a spectrophotometric study of the reaction that hydroxyl ion reacts with both the colored phenolphthalein ion and a colorless lactoid phenolphthalein ion to produce the triply charged carbinol.

Lund<sup>5</sup> measured the rate of fading of phenolphthalein at various sodium hydroxide and sodium chloride concentrations, and properly ascribed the increase in molar rate constant with

increasing sodium hydroxide to a Brönsted primary salt effect.<sup>6</sup> He employed the Brönsted-Debye Limiting Law (B. D. L. L.) as a means of determining the number of charges on the reactant phenolphthalein ion from the quantitative dependence of the rate of reaction upon the concentration.

However, on plotting his data for  $\log k_1$ , against the square root of the ionic strength,  $\sqrt{\mu}$ , he obtained the surprising result that the limiting slope was unity. This slope is one-half that required by the B. D. L. L. for a reaction between an ion of charge  $-2$  and a hydroxyl ion. Since the B. D. L. L. has been abundantly confirmed in all cases where the charge type is definitely known, one would be forced to conclude that the reactant ion of phenolphthalein has a charge of  $-1$  instead of  $-2$ .

This behavior became even more anomalous when LaMer and Amis<sup>7</sup> demonstrated that the B. D. L. L. was obeyed precisely for the rate of carbinol formation of Brom Phenol Blue (B. P. B.). The theoretical limiting slope of two (2.02) which was obtained shows that the reactant B. P. B. ion possesses a charge of  $-2$ . Phenolphthalein and B. P. B. are structurally similar. Aside from bromine substitution in the phenolic rings and the presence of a sulfonic acid instead of a carboxylic acid radical they possess identical triphenylmethane structures.

The two dyes differ, however, in color and acidic properties. B. P. B. is a relatively strong acid which dissociates hydrogen ions in a dilute or weakly acid solution whereas phenolphthalein is a much weaker acid which dissociates hydrogen ions only in alkaline solution as shown by the titration curve in Fig. 1. The estimated value of  $K_1/K_2 \approx 4$  from the titration curve is in accord with the colorimetric determinations of the ratio.<sup>8</sup> We also find that a red color appears on the addition of less than 0.10 mole of hydroxyl ion per mole of phenolphthalein. At first sight this observation might be taken as indicating a charge of less than 2 for the red ion.

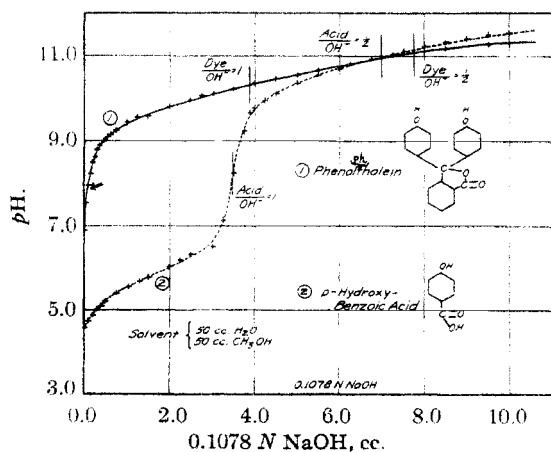


Fig. 1.

- (1) A. von Baeyer, *Ann.*, **202**, 36 (1880).
- (2) Kober and Marshall, *This Journal*, **33**, 50 (1911).
- (3) Biddle and Porter, *ibid.*, **37**, 1571 (1915).
- (4) Thiel and Jungfer, *Z. anorg. Chem.*, **175**, 62 (1920).
- (5) Lund, *J. Chem. Soc. (London)*, 1844 (1930).

- (6) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925); LaMer, *Chem. Rev.*, **10**, 179 (1932); *J. Franklin Institute*, **225**, 709 (1938).
- (7) LaMer and Amis, *This Journal*, **61**, 905 (1939).
- (8) Rosenstein, *ibid.*, **34**, 1117 (1912).

Bury's resonance theory,<sup>9</sup> however, requires that the colored form of phenolphthalein should have a charge of  $-2$ . This is clearly inconsistent with Lund's data which we have been unable to reconcile with the requirements of the theory by recalculation. The data of Lund are inadequate to establish the mechanism of carbinol formation for phenolphthalein since the equilibrium constant was not measured in order to obtain  $k_1$  from  $k_1' + k_2$  by a rigorous mathematical method. The present investigation has been undertaken to determine the charge of the reacting ion from the Brönsted-Debye limiting law and to establish experimentally a mechanism for this carbinol formation which is consistent with well established electrostatic and kinetic principles.

### Experimental

A Coleman Double Monochromator Photoelectric Spectrophotometer (Model 10-S) was used to measure the transmittances of the colored solutions. The transmittance measurements are accurate to  $\pm 0.1\%$ . The instrument was equipped with specially designed water-jacketed absorption cells (cuvettes) for accurate temperature control. The wave-length scale was calibrated against a didymium glass filter using a slit of 30  $m\mu$  width.

Phenolphthalein was twice recrystallized from absolute methanol, m. p. 261–262° (cor.). The absorption maximum was 550  $m\mu$ . The stock solution for the fading runs consisted of 0.1721 g. of phenolphthalein in 100 cc. of 50% aqueous ethanol solution. For the regeneration reactions 0.1721 g. of phenolphthalein was dissolved in 100 cc. of 1 *M* NaOH and used after at least one hour and not more than eight hours. This carbinol solution was pale pink initially, due to traces of unfaded phenolphthalein, but after about twelve hours showed an increasing absorption at 425  $m\mu$ , indicating some further reaction. All regeneration experiments were accordingly made on freshly prepared solutions.

Sodium hydroxide solutions were prepared by the method of Sørensen<sup>10</sup> and stored in paraffin-lined bottles protected from carbon dioxide. They were standardized against B. of S. potassium acid phthalate and showed 0.4% residual carbonate by a differential titration.

Neutral sodium chloride solutions were employed.

The temperature was maintained constant to  $\pm 0.005^\circ$  and standardized against a B. of S. platinum resistance thermometer.

Calibrated hypodermic syringes<sup>11</sup> were used to deliver small quantities of reagents accurately.

In a typical fading experiment 1 cc. of phenolphthalein stock solution was added to approximately 499 cc. of sodium hydroxide solution of such a strength that a concentration of 0.006 to 0.02 *M* sodium hydroxide was obtained on making up to volume. The solution was mixed rapidly and an absorption cell filled therewith.

The remaining solution was placed in a paraffin-lined paper milk container in the thermostat. The measurements of the transmittance of the solution which required approximately one and one-half minutes each, were made every fifteen minutes over a period of about three hours. The cuvette with water circulating around it continuously was replaced in the thermostat between observations.

The regeneration runs were made by diluting 1 cc. of stock solution with dilute sodium hydroxide of such strength that concentrations of 0.006 to 0.020 *M* were obtained on making up to volume.

A Beckmann *pH* meter was used to measure *pH*'s. No correction for sodium ion was made. The glass electrode yielded stable readings in the alcohol-water solution.<sup>12</sup>

**Calculation of Rate and Equilibrium Constants.**—The differential expression describing the rate of fading formulated in (1) is

$$-d[R^-]/dt = k_1[OH^-][R^-] - k_2[\text{carbinols}] \quad (2)$$

where "carbinols" is written instead of  $ROH^\equiv$  to indicate the possibility of a mixture of carbinols in solution. The concentration of hydroxyl ion,  $[OH^-]$ , being sensibly constant during the course of a run, the reaction follows a first order course. For convenience in treating the data,  $k_1'$  was set equal to  $k_1[OH^-]$ . The concentration (*C*) of dye at any moment is related to the transmittance (*T*) by Beer's law

$$C = k_B \log T \quad (3)$$

For a reversible pseudo-unimolecular reaction, integration of (2) gives

$$k_1' + k_2 = \frac{2.303}{t} \log \left( \frac{c_e}{c_e - c} \right) \quad (4)$$

where  $c_e$  is concentration of carbinols at equilibrium and  $c$  is concentration of carbinols at time  $t$ . Substitution of equation (3) in (4) gives

$$k_1' + k_2 = \frac{2.303}{t} \log \left[ \frac{\log T_{t=0} - \log T_t}{\log T_t - \log T_e} \right] \quad (4a)$$

where  $T_{t=0}$ ,  $T_t$ ,  $T_e$  are, respectively, the transmittance for time zero, time  $t$  and equilibrium. The complex reaction velocity constant  $k_1' + k_2$  is given by the slope of the curve obtained by plotting time in minutes against  $\log (\log T_t - \log T_e)$  and was proven to be independent of the direction from which equilibrium is approached.

The equilibrium constant is calculated from

$$K_C = \frac{[\text{Carbinols}]}{[R^-][OH^-]} = \frac{[\log T_{t=0} - \log T_e]}{[\log T_t][OH^-]} \quad (5)$$

The concentration of carbinols is the difference in concentration of colored ion initially (when none has faded) and at equilibrium. This value is the ordinate obtained by extrapolating the plot of equation (4) to zero time.

(9) Bury, *THIS JOURNAL*, **57**, 2115 (1935).

(10) Sørensen, *Biochem. Z.*, **21**, 168 (1909).

(11) Chaney, *Ind. Eng. Chem., Anal. Ed.*, **10**, 326 (1938).

(12) S. T. Schickelanz and A. D. Etienne, *Ind. Eng. Chem.*, **29**, 157 (1937).

Values of the molar rate constant are calculated from

$$k_1 = \frac{k_1 + k_2}{[\text{OH}^-] + 1/K_c} \quad (6)$$

### Results

The colored form of phenolphthalein obeys Beer's law over the range of concentrations considered in this investigation: namely, up to  $1.34 \times 10^{-5}$  m./l. (Table I). The values of  $T_t = 0$  are extrapolated values since concentrations of hydroxyl ion, insufficient to convert all phenolphthalein to the colored ion, are sufficient to cause appreciable fading of the latter during the time of observation. The value of  $k_B = -1.63 \times 10^{-5}$  m./l. is considered the most accurate, being measured from a specially purified sample of phenolphthalein. The molar extinction coefficient ( $E = \frac{1}{Cl} \log(I_0/I)$ ) is  $0.3057 \times 10^{-5}$  ( $l = \text{length}$ ) (7).

TABLE I

MOLAR EXTINCTION COEFFICIENTS ( $E$ ) AND CONSTANTS FOR BEER'S LAW ( $k_B$ ) FOR ALKALINE PHENOLPHTHALEIN SOLUTIONS

NaOH = 0.014 M,  $\lambda = 550$  m $\mu$ , temp. = 25°, layer thickness = 20.054 mm.

Concn. dye, $\times 10^5$ m./l.	$k_1 + k_2$ , min. <sup>-1</sup>	$T_{t=0}$ , %	$E$ , (m./l.) <sup>-1</sup> cm. <sup>-1</sup> $\times 10^{-5}$	$k_B \times 10^5$ , m./l.
0.670	0.01209	39.60	0.2992	1.664
1.102	.01195	21.10	.3057	1.630
1.340	.01207	15.75	.2987	1.668

A typical run is given in Table II and plotted in Fig. 2. Equilibrium transmittances measured

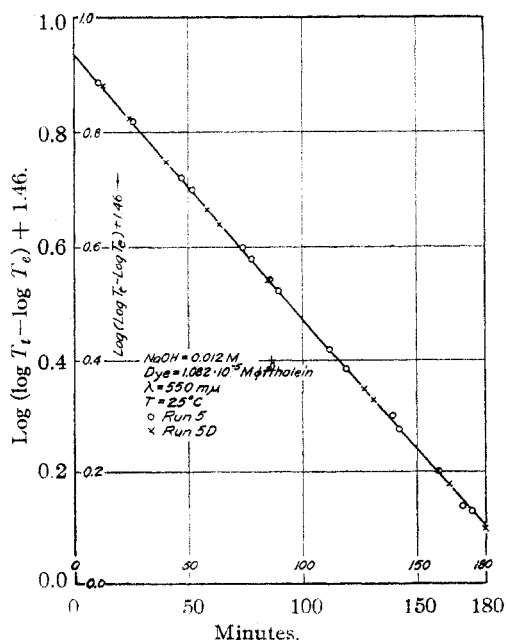


Fig. 2.

after twenty-four hours were stable and no irreversible fading<sup>13</sup> was observed. Extrapolated values of  $T_{t=0}$  are shown in Table III. The constancy of these extrapolated values over the pH range employed in this study shows that no secondary salt effect is detectable.

TABLE II  
TYPICAL RUN

NaOH = 0.012 M,  $\lambda = 550$  m $\mu$ , dye =  $1.102 \times 10^{-5}$  M, thickness of layer 20.054 mm.

Min.	% T	$k' + k_2 \times 10^2$ , min. <sup>-1</sup>	$k_1 \times 10^2$ , min. <sup>-1</sup>	$k_2 \times 10^2$ , min. <sup>-1</sup>
0	(21.2)			
11.17	22.9	1.069	39.5	0.5943
25.58	25.0	1.071	39.6	.5956
46.83	27.8	1.069	39.5	.5943
52.00	28.4	1.064	39.4	.5916
73.93	30.8	1.059	39.2	.5889
78.00	31.25	1.065	39.4	.5919
85.58	32.0	1.065	39.4	.5923
89.83	32.4	1.066	39.4	.5926
112.58	34.2	1.054	39.0	.5862
119.33	34.8	1.067	39.5	.5935
139.58	36.0	1.051	38.9	.5845
142.33	36.3	1.068	39.5	.5938
159.67	37.1	1.051	38.9	.5840
170.08	37.8	1.078	39.9	.5994
174.33	37.95	1.073	39.7	.5964
	42.2			
	Mean	1.065	39.40	.5920
		a.d. = 0.46%		
		A.D. = 0.14%		

TABLE III

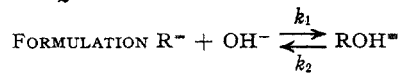
THE INDEPENDENCE OF TRANSMITTANCES EXTRAPOLATED TO ZERO TIME UPON THE CONCENTRATION OF NaOH

Dye =  $1.102 \times 10^{-5}$  M;  $\lambda = 550$  m $\mu$ ; layer thickness = 20.054 mm.

NaOH $\times 10^3$	$T_{t=0}$ , %	$k_B \times 10^5$
6	21.38	1.64
8	21.32	1.64
10	21.27	1.64
12	21.21	1.64
14	21.10	1.63
16	21.24	1.63
20	21.16	1.64

TABLE IV

RATE AND EQUILIBRIUM CONSTANTS FOR THE SIMPLE



$\lambda = 550$  m $\mu$ ,  $T = 25^\circ$

NaOH $\times 10^3$	$k' + k_2$ , min. <sup>-1</sup> $\times 10^2$	K	min. <sup>-1</sup> $\times 10^2$	min. <sup>-1</sup> $\times 10^2$
6	0.7568	61.78	34.12	0.5522
8	.856	63.60	36.09	.5674
10	.9638	65.25	38.06	.5832
12	1.067	66.52	39.47	.5951
14	1.195	67.86	41.59	.6128
16	1.331	69.06	43.66	.6322
20	1.622	71.00	47.59	.6702

(13) Thiel and Coch, *Z. anorg. allgem. Chem.*, **217**, 254-256 (1934)

Table IV summarizes the molar rate and equilibrium constants, which are reliable to better than 1%. The increase in these constants with concentration is shown in Table V to be due to a primary salt effect.<sup>14</sup>

**Discussion**

The theory assumes that the kinetics of the reaction may be formulated as  $R^{\ominus} + OH^{\ominus} \rightleftharpoons X^{\ominus} \rightarrow ROH^{\ominus}$  where  $X^{\ominus}$  is the activated complex sensibly in equilibrium with the reactants but not with the product. The influence of the charges of the reactant species and the ionic strength of the solution is given by the Brönsted-Debye limiting law equation (B. D. L. L.)

$$\log k_1 = \log k_0 + 1.02 Z_R - Z_{OH} - \sqrt{\mu} \quad (8)$$

where  $k_0$  is the extrapolated molar rate constant for zero ionic strength.

The equilibrium constant is given by the expression

$$K_a = \frac{a_R - a_{OH^{\ominus}}}{a_{ROH^{\ominus}}} = \frac{C_R - C_{OH^{\ominus}}}{C_{ROH^{\ominus}}} \frac{f_R - f_{OH^{\ominus}}}{f_{ROH^{\ominus}}} \quad (9)$$

where  $a$  is activity and  $c$  is concentration. Introducing the Debye-Hückel limiting equation for the activity coefficient ( $f$ ), yields for the measured stoichiometric constant  $K_C$

$$\log K_C = \log K_a + 1.02 Z_R - Z_{OH} - \sqrt{\mu} \quad (10)$$

Figure (3) shows a plot of  $\log k_1$  against  $\sqrt{\mu}$ . The ionic strength is varied in one series of runs (circles) by increasing the concentration of sodium hydroxide, in the other (crosses) by increasing the concentrations of sodium chloride. A limit-

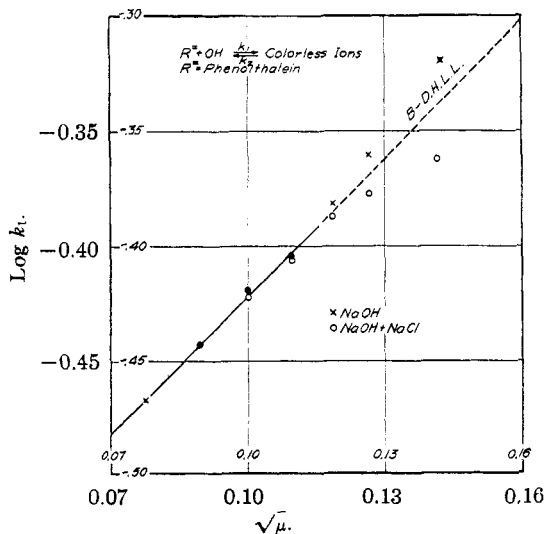


Fig. 3.

(14) For review see V. K. LaMer, *Chem. Rev.*, 10, 179 (1932).

ing slope of +2 is obtained in accord with formulation (1) and Eq. (8) showing conclusively that carbinol formation in phenolphthalein involves the reaction of an ion of charge  $-2$  with the hydroxyl ion. The forward rate exhibits no anomalous behavior.

The upper curve in Fig. 4 shows the plot of  $\log K_C$  against  $\sqrt{\mu}$ . The slope is unity or one-half the value required by the theory for an equilibrium involving doubly charged phenolphthalein, hydroxyl and triply charged carbinol ions. This abnormal behavior has been attributed erroneously by Lund to the variation of the forward rate constant with ionic strength. Failure to measure the equilibrium constant in sufficiently dilute solutions is responsible for this misunderstanding.

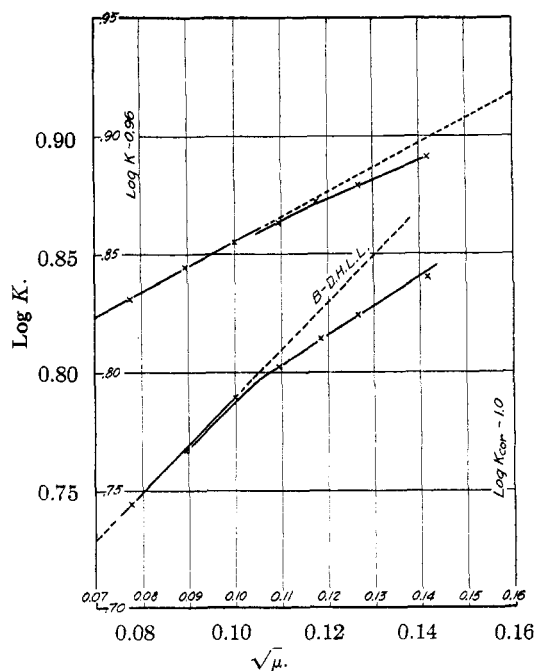
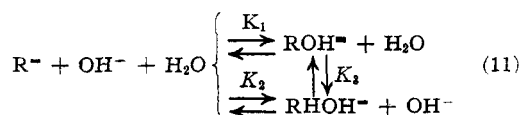


Fig. 4.

The abnormal behavior arises from the fact that the concentration of the triply charged carbinol assumed in (1) cannot be measured directly as is assumed in formulation (1). Over the pH range covered in these experiments (11.8 to 12.3) and particularly at the lower concentration of alkali the triply charged carbinol should be partially hydrolyzed. The equilibrium relationships under such conditions may be formulated



where  $\text{RHOH}^-$  is also a colorless carbinol. The equilibrium described by  $K_1$  considers the triply charged carbinol as the product in equilibrium with reactants  $\text{R}^-$  and  $\text{OH}^-$ . This equilibrium constant is shown by (10) to be affected by the ionic strength.  $K_2$ , however, which considers the doubly charged carbinol and hydroxyl ion in equilibrium with the reactants, is not affected by the ionic strength.  $K_3$  describes the mobile equilibrium existing between these carbinols and is defined as

$$K_3 = \frac{[\text{ROH}^{\ominus}][\text{H}_2\text{O}]}{[\text{RHOH}^{\ominus}][\text{OH}^-]} \quad (12)$$

On the basis of this equilibrium formulation,  $K_C$  calculated from the data may be separated into  $K_{1a}$  and  $K_2$  ( $K_{2a} = K_{2c}$ ). Consideration of (5) and (6) shows that this operation does not affect the calculated values of  $k_1$  which have been shown to obey precisely the predictions of the Brönsted-Debye equation. The separation of  $K_C$  into  $K_{1a}$  and  $K_2$  is shown by the equations

$$K_C = \frac{[\text{ROH}^{\ominus}] + [\text{RHOH}^{\ominus}]}{[\text{R}^-][\text{H}_2\text{O}][\text{OH}^-]} = \frac{[\text{ROH}^{\ominus}]}{[\text{R}^-][\text{H}_2\text{O}][\text{OH}^-]} + \frac{[\text{RHOH}^{\ominus}]}{[\text{R}^-][\text{H}_2\text{O}][\text{OH}^-]} \quad (13)$$

$$K_C = K_{1a}10^2\sqrt{\mu} + K_2/[\text{OH}^-] \quad (14)$$

TABLE V

RATE AND EQUILIBRIUM CONSTANTS ( $\text{R}^- + \text{OH}^- \rightleftharpoons \text{ROH}^{\ominus}$ ) IN NaOH AND NaCl SOLUTIONS

T = 25°						
NaOH × 10 <sup>3</sup>	NaCl × 10 <sup>3</sup>	μ × 10 <sup>3</sup>	k <sub>1</sub> + k <sub>2</sub> min. <sup>-1</sup> × 10 <sup>2</sup>	K <sub>C</sub>	k <sub>1</sub> min. <sup>-1</sup> × 10 <sup>2</sup>	k <sub>2</sub> min. <sup>-1</sup> × 10 <sup>2</sup>
6	0	6	0.7568	61.78	34.12	0.5522
6	2	8	.7794	63.99	36.05	.5634
8	0	8	.8500	63.60	36.09	.5674
8	2	10	.8819	65.20	37.80	.5800
8	4	12	.9065	66.41	39.33	.5944
8	6	14	.9242	68.36	40.86	.5977
8	8	16	.9359	70.27	42.10	.5991
8	12	20	.9411	73.43	43.55	.5930

A test of equation (14) is made by selecting values for  $K_{1a}$  and  $K_2$  and calculating  $K_C$  at different hydroxyl ion concentrations. Comparison of  $K_C$  calculated from experimental data and  $K_C$  calculated from equation (14), employing  $K_{1a} = 40.25$  and  $K_2 = 0.038$ , is shown in Table VI. The agreement is within experimental error over the range where the Debye-Hückel limiting equation is valid.

Graphically the behavior of  $K_{1a}$  expressed in concentrations is shown in the lower curve in Fig. 4.  $K_{1a}$  is obtained by solving equation (14)

TABLE VI

EQUILIBRIUM CONSTANTS (EQS. (13) AND (14)): $K_C =$ EXPERIMENTAL EQUILIBRIUM CONSTANT; $(K_C)_{14} =$ EQUILIBRIUM CONSTANT CALCULATED FROM (14)			
NaOH × 10 <sup>3</sup>	$K_C$	$(K_C)_{14}$	$\Delta K_C, \%$
6	61.78	62.40	1.0
8	63.60	63.52	0.13
10	65.25	64.98	.43
12	66.52	66.56	.06
14	67.86	68.24	.56
16	69.06	69.87	1.2
20	71.00	73.10	2.8

employing experimental values of  $K_C$  and hydroxyl ion and the value of 0.038 for  $K_2$ . The Brönsted-Debye equation is obeyed over the range of dilute solution up to  $\sqrt{\mu} = 0.11$ . The close agreement of the experimental  $K_C$  with the  $K_C$  calculated from (14) confirms the postulated equilibria.

The ionization constant of  $\text{RHOH}^-$  may be calculated from (12) and the values of  $K_{1a}$  and  $K_2$ . Using  $K_{1a} = 40.25$ ,  $K_2 = 0.038$  and the ion constant for water  $K_W = 1 \times 10^{-14}$  (at 25°) the value of the ionization constant is  $1.1 \times 10^{-11}$ .

### Summary and Conclusions

1. The kinetics of the reaction of phenolphthalein with hydroxyl ion to produce a colorless carbinol have been investigated spectrophotometrically at 25° for sodium hydroxide solutions (0.006 to 0.020 M) with and without the addition of sodium chloride.

2. Precise values of the transmittances of phenolphthalein solution at 550 mμ have been obtained by extrapolating to zero time. The extinction coefficient is independent of the concentration of alkali showing that no perceptible secondary salt effect exists at these concentrations.

3. The limiting slope of the log  $k_1$  (forward rate constant) vs. the square root of ionic strength,  $\sqrt{\mu}$  establishes that carbinol formation involves the reaction of a doubly charged negative phenolphthalein ion with a hydroxyl.  $\text{R}^- + \text{OH}^- \rightarrow \text{carbinol}$ .

4. The limiting slope of log  $K$  (equilibrium constant) vs.  $\sqrt{\mu}$  is one-half that predicted for the simple formulation  $\text{R}^- + \text{OH}^- \rightleftharpoons \text{ROH}^{\ominus}$ . An interpretation consistent with established electrostatic principles is obtained on the assumption that the carbinol is partially hydrolyzed, viz.,  $\text{ROH}^{\ominus} + \text{H}_2\text{O} \rightleftharpoons \text{RHOH}^{\ominus} + \text{OH}^-$ .