The final isobutylene fraction (b. p. about −6°) dissolved completely in 63% sulfuric acid solution.

Summary

Isobutylene, when decomposed at 650° to the extent of 0.1–1.0%, gives rise to methane, propylene and ethylene as the only gaseous reaction products. The fact that ethylene persists even at 0.1% conversion emphasizes the need for caution in interpreting the "initial products of reaction" by the zero-extrapolation method.

EVANSTON, ILLINOIS RECEIVED JULY 19, 1937

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Reaction of Brom Phenol Blue, Iodo Phenol Blue and Chlor Phenol Blue with Hydroxyl Ion[1]

BY FRANK W. PANEPINTO AND MARTIN KILPATRICK

In the study of the dissociation constants of indicators it has been shown that brom phenol blue reacts with hydroxyl ion to give a colorless solution.[2] This paper presents the results of a study of this reaction and the reaction of tetrachloro- and tetraiodophenolsulfonphthaleins with hydroxyl ion. From a study of the kinetic electrolyte effect it will be shown that the reaction is between the bivalent anion and the hydroxyl ion.

Experimental Part

The indicators used in this study were specially purified products.[3]

Analysis gave the following:

	M. p. °C corr.	Found, %	Calcd., %
Tetrabromophenolsulfonphthalein (Brom phenol blue)	270–271	S, 4.55 Br, 47.76	4.77 47.73
Tetraiodophenolsulfonphthalein (Iodo phenol blue)	259–260	I, 59.05	59.12
Tetrachlorophenolsulfonphthalein (Chlor phenol blue)	255	Cl, 28.70	28.80

Stock solutions of the indicators were prepared by dissolving the acid in alcohol, adding sufficient carbonate-free sodium hydroxide to form the monosodium salt, evaporating off the alcohol and dissolving the salt in water. All stock solutions were approximately 2 × 10^{-4} molar and were diluted tenfold for the experiments. The reaction was followed by measuring the disappearance of the blue color by means of a Duboscq colorimeter. All solutions were referred to standard solutions which were freshly prepared from stock solutions. The experiments were carried out in a thermostat regulated to ±0.005° and the solutions were protected from light except during the transfer of samples for analysis. All salts were C. P. products purified by crystallization.

Preliminary experiments had shown that the rate of disappearance of the blue color followed the monomolecular law[2] as shown in Table I.

TABLE I

FADING OF BROM PHENOL BLUE AT 30°

	NaOH (moles per liter) 0.009		0.005	
Days	k	k_1	k	k_1
0.875	0.590	65.5	0.287	57.3
1.0	.585	64.9	.298	59.6
1.167	.581	64.5	.290	58.0
1.875	.574	63.8	.302	60.5
2.17	.578	64.2	.295	59.0
2.83	.592	65.6	.299	59.8
3.0	.583	64.8	.285	57.0
3.167	.566	62.8	.305	60.9
	Average	64.5		
3.83			0.286	57.1
4.0			.293	58.7
4.83			.288	57.5
5.0			.303	60.6
5.21			.290	57.9
6.0			.295	59.0
6.17			.299	59.7
6.83			.297	59.3
7.0			.285	57.0
7.83			.302	60.4
8.0			.300	60.0
			Average	58.9

The velocity constant k is calculated from the equation $k = 2.30/t \log a/(a-x)$ where a represents the initial concentration of the bivalent anion, $a-x$ the concentration at time t. The unit of time is the day. From Table I it is seen that the reaction at constant hydroxyl ion concentration follows the monomolecular law and from

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(1) Abstracted from the dissertation of Frank W. Panepinto presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1937.

(2) Chase and Kilpatrick, THIS JOURNAL, **54**, 2284 (1932); Kilpatrick, *Chem. Rev.*, **16**, 57 (1935).

(3) The authors take this opportunity to acknowledge the kindness of Dr. W. C. Harden of Hynson, Westcott and Dunning Co. in supplying these indicators.

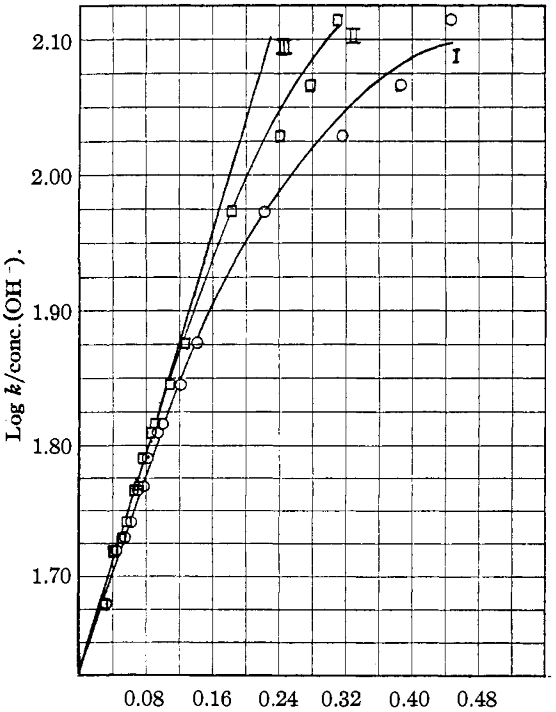
the value of $k_1 = k/C_{OH^-}$ it is evident that although the rate is approximately proportional to the hydroxyl ion concentration the values of k increase with increasing sodium hydroxide concentration. This is confirmed by the results summarized in Table II.

TABLE II

EXPERIMENTS WITH BROM PHENOL BLUE AT 30°

NaOH, m./l.	k_1	Av. value k_1
0.001	48.4	
	47.6	
	48.0	48.0
.002	52.3	
	52.5	52.4
.003	53.7	53.7
.004	55.2	
	55.1	55.2
.005	58.9	
	58.5	58.7
.006	58.8	
	59.0	58.9
.007	62.1	62.1
.008	63.3	63.3
.009	64.5	
	64.6	64.6
.010	65.5	65.5

In order to determine whether this was an electrolyte effect, experiments were carried out in the presence of neutral salts. Table III summarizes the experiments.



I, ○ vs. $\sqrt{\mu}$. II, □ vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$. III, Slope = 2.00.

Fig. 1.—Effect of electrolyte concentration: from phenol blue at 30°.

TABLE III

ELECTROLYTE EFFECT AT 30°

NaOH, m./l.	NaCl, m./l.	k_1
0.002	0.001	53.7
.002	.005	62.0
.001	.009	65.4
.005	.045	94.3
.009	.041	94.8
.005	.095	98.3
.005	.095	106.5
.009	.091	111.0
.009	.091	113.7
.009	.091	115.6
.005	.145	116.1
.009	.141	117.1
.005	.195	130.0
.009	.191	130.1
	KBr, m/l.	
0.005	0.045	94.2
.009	.041	93.7
.009	.191	130.5
.005	.195	130.0
.004	.001	58.0
.005	.002	61.9
.004	.006	65.5
.005	.010	70.1
.003	.017	75.1
.005	.015	75.1
.005	.045	93.7
.009	.041	94.4
.005	.195	129.3

The results summarized in Tables II and III are presented graphically in Fig. 1 (average values in the graph), log k_1 being plotted against $\sqrt{\mu}$ and $\sqrt{\mu}/(1 + \sqrt{\mu})$. The slope of the lines is two which means that the z_Az_B product in the equations

$$\log k_1 = \log k_0 + z_Az_B \sqrt{\mu} \qquad (1)$$

$$\log k_1 = \log k_0 + z_Az_B \sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (2)$$

is two. Since one of the reactants is the hydroxyl ion the other must be negatively charged and bivalent. From this we conclude that the reaction is between the bivalent anion of the dibasic indicator acid and the hydroxyl ion. The experimental test of equation (2) is given in Table IV.

The equation holds up to 0.020 μ and the results can be expressed to 0.200 μ by the introduction of a term linear in the concentration. The experimental results are expressed by the equation

$$\log k_1 = \log k_0 + 2.06 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + 0.69C \qquad (3)$$

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(4) For the use of the second equation see Kilpatrick, THIS JOURNAL, 56, 2326 (1934).

where C represents the electrolyte concentration in moles per liter.

TABLE IV

TEST OF EQUATION 2

μ	k_1	Log k_0	Average Log k_0	Average k_0
0.001	48.0	1.625		
.002	52.3	1.636		
.003	53.7	1.633		
.004	55.2	1.628		
.005	58.3	1.639		
.006	58.8	1.630		
.007	62.0	1.643		
.009	64.5	1.642		
.010	65.5	1.639		
.015	70.2	1.633		
.020	75.1	1.633	1.635	43.1
.050	94.0	1.612		
.100	107.1	1.554		
.150	116.6	1.512		
.200	130.0	1.499		

The concentration of halide in the colorless solution was determined and found to correspond to one bromide ion appearing per molecule of brom phenol blue disappearing. It was not convenient to follow the reaction by the appearance of such small amounts of bromide in the solution but the stoichiometric relationship was tested with more concentrated solutions. The results for brom phenol blue are summarized in Table V.

TABLE V

HALIDE IN FADED BROM PHENOL BLUE SOLUTIONS

No.	Indicator concn. m./l.	Halide (g. Br) Volumetric	Gravimetric	Theoretical on basis of one Br
1	2×10^{-4}	....	0.0024	0.0017
2	2×10^{-4}	....	.0014	.0017
3	2×10^{-4}	....	.0017	.0017
4	2×10^{-4}	0.0017	....	.0017
5	2×10^{-4}	.0017	....	.0017
6	2×10^{-4}	.0016	....	.0017
7	2×10^{-4}	.0016	....	.0017
8	2×10^{-4}	.0017	....	.0017
9	2×10^{-4}	.0016	....	.0017
10[a]	1.9×10^{-5}	.00018	....	.00015
11[a]	1.6×10^{-5}	.00014	....	.00013
12[a]	1.5×10^{-5}	.00014	....	.00012
13[b]	2×10^{-5}	....	.0002	.0003
14	1×10^{-4}	.0008	.0010	.0008
15	1×10^{-4}	.0012	.0012	.0008
16	1×10^{-4}	.0012	.0010	.0008
17	1×10^{-4}	.0012	.0010	.0008
18	1×10^{-4}	.0012	.0010	.0008
19	1×10^{-4}	.0015	.0010	.0008
20[b]	1×10^{-4}	.0021	.0023	.0017
21	1×10^{-4}	.0012	.0012	.0008

[a] Concentrations calculated from the colorimetric reading. [b] 200 cc. of sample used. All others, 100 cc. All samples except those marked [a] were colorless.

In order to determine the effect of electrolyte concentration on the energy of activation, measurements were carried out at 20 and 25°. The results are summarized in Table VI.

TABLE VI

EFFECT OF TEMPERATURE

NaOH m./l.	k_1 (20°)		k_1 (25°)	$\frac{k_{25}}{k_{20}}$	E_A, kcal. 20–25	E_A, kcal. 25–30
0.000	21.2[a]		30.3[a]	1.42	12.2	12.6
.001	24.4		34.8	1.43	12.4	11.6
.002	26.0		36.8	1.41	11.9	12.6
.003	27.1		38.3	1.41	11.9	12.1
.004	28.0		39.1	1.40	11.7	12.3
.005	28.8		41.0	1.42	12.2	12.6
.006	29.2		41.4	1.42	12.2	12.6
.007	30.5		43.2	1.42	12.2	12.8
.008	30.8		44.0	1.43	12.4	..
.009	31.7		44.7	1.41	11.9	13.6
.010	31.9		45.7	1.43	12.3	12.8
.010 .005 NaCl	35.0	0.005 NaOH .010 NaCl	49.6	1.42	12.2	12.3
.010 .010 NaCl	37.3	.005 NaOH .015 NaCl	53.0	1.42	12.2	12.6
.008 .042 NaCl	46.0	.005 NaOH .045 NaCl	65.4	1.42	12.2	13.1
.007 .093 NaCl	55.2	.005 NaOH .095 NaCl	77.9	1.41	11.9	11.0
.006 .144 NaCl	61.3	.005 NaOH .145 NaCl	83.5	1.41	11.9	12.1
.006 .194 NaCl	64.0	.005 NaOH .195 NaCl	87.9	1.42	12.2	14.1
				Av.	12.1	12.5
				a. d.	0.2	0.5

[a] Values obtained by extrapolation using equation 2.

Experiments with Chlor Phenol Blue and Iodo Phenol Blue.—The experiments with chlor phenol blue and iodo phenol blue were carried

TABLE VII

REACTION OF CHLOR PHENOL BLUE WITH HYDROXYL ION

μ	k_1 (30°)	k_1 (25°)	k_1 (20°)	E_A, kcal. 30–25	E_A, kcal. 25–20
0.000	52.6[a]	37.4[a]	25.5[a]	12.1	13.1
.001	59.6	42.7	29.3	11.6	13.1
.002	64.3	46.0	31.5	12.1	12.4
.003	66.2	47.0	32.2	12.3	13.1
.004	67.1	48.9	33.8	11.3	12.9
.005	70.5	51.0	35.0	11.6	13.1
.006	72.4	51.7	35.9	12.1	12.7
.007	73.6	53.1	36.1	11.6	13.4
.008	76.6	53.6	37.2	12.8	12.7
.009	77.6	55.8	38.2	11.8	13.1
.010	79.3	56.7	38.6	11.8	13.4
.015	86.7	61.1	42.2	12.3	12.9
.020	91.7	65.7	45.3	12.1	12.9
.050	113.5	81.0	58.2	12.1	11.4
.100	129.5	95.9	67.1	11.0	12.4
.150	134.9	103.3	72.4	9.4	12.2
.200	142.2	106.4	74.1	10.2	12.7
			Av.	11.6	12.7
			a. d.	0.6	0.4

[a] Values obtained by extrapolation using equation 2.

out in similar fashion. The results are summarized in Tables VII and VIII.

TABLE VIII

REACTION OF IODO PHENOL BLUE WITH HYDROXYL ION

μ	k_1 (30°)	k_1 (25°)	k_1 (20°)	E_A, kcal. 30–25	E_A, kcal. 25–20
0.000	20.1[a]	14.3[a]	10.0[a]	12.1	12.1
.001	23.0	16.3	..	12.3	..
.002	24.6	17.3	12.4	12.6	11.4
.003	25.7	18.1	12.7	12.6	12.2
.004	26.3	..	..	..	..
.005	27.4	19.3	13.6	12.6	12.2
.006	27.6	19.7	..	12.1	..
.007	28.5	20.5	..	11.8	..
.008	28.9	..	14.6	..	..
.009	29.8	21.2	..	12.1	..
.010	30.0	21.6	15.2	11.8	12.2
.015	..	23.4	16.4	..	12.2
.020	34.8	25.0	17.6	11.8	12.2
.050	44.8	31.5	22.1	12.6	12.2
.100	50.8	35.5	26.0	12.8	10.7
.150	54.3	38.2	27.4	12.6	10.9
.200	57.2	41.0	28.4	11.8	12.7
			Av.	12.3	11.9
			a. d.	0.2	0.5

[a] Values obtained by extrapolation using equation 2.

The experiments up to $\mu = 0.006$ were with sodium hydroxide while those at higher ionic strengths were in the presence of sodium chloride and potassium bromide at various concentrations. Determinations of halide again showed that for every colored molecule disappearing, one bromide ion appeared in the solution. At 30° the results can be represented by the equation

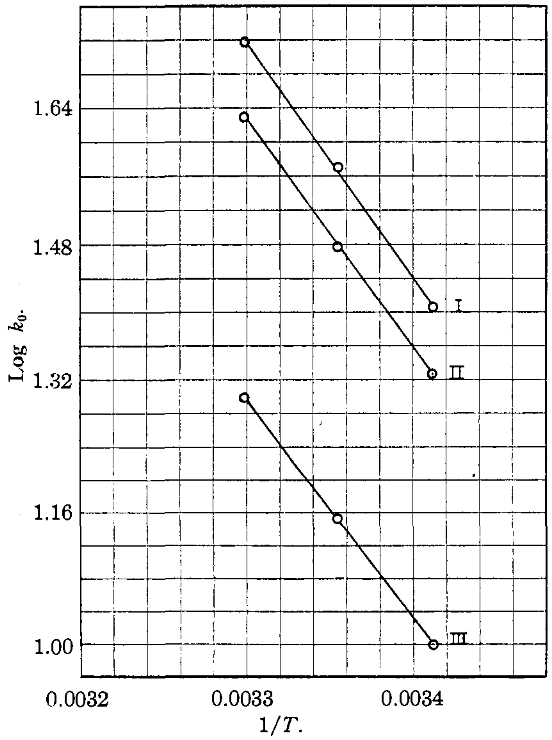

Fig. 2.—Effect of temperature: I, chlor phenol blue; II, brom phenol blue; III, iodo phenol blue.

$$\log k_1 = \log k_0 + 2.06 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + 0.81C \qquad (4)$$

The results at 30° can be represented by the equation

$$\log k_1 = \log k_0 + 2.06 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + 0.66C \qquad (5)$$

The order of the velocity constants is chlor phenol blue > brom phenol blue > iodo phenol blue.

It is interesting to note that some reactions involving organic halides and hydroxyl ion give the reverse order of stability to that found for the fading reaction. For example, the reaction between alkyl halides and potassium hydroxide studied by Grant and Hinshelwood has the following values for the velocity constants

for alkyl chloride $k = 0.793 \times 10^{11} \sqrt{T} e^{-23{,}000/RT}$
for alkyl bromide $k = 1.28 \times 10^{11} \sqrt{T} e^{-21{,}000/RT}$
for alkyl iodide $k = 2.70 \times 10^{11} \sqrt{T} e^{-21{,}000/RT}$

The reason given for the relatively higher rate of reaction by the iodide is that the energy of activation is relatively lower. This same reasoning does not account, however, for the lower "k" for the alkyl bromide although the energy of activation is identical with that of the iodide.

Figure 2 indicates that the energies of activation do not differ greatly. The results at zero ion concentration can be represented by the equations of the form

$$\ln k = B - (E_A/RT)$$

For iodo phenol blue

$$\ln k = 11.59 - (12{,}100/RT) \qquad (6)$$

for brom phenol blue

$$\ln k = 12.85 - (12{,}400/RT) \qquad (7)$$

for chlor phenol blue

$$\ln k = 13.39 - (12{,}600/RT) \qquad (8)$$

The velocity constants are in the units liters per gram molecule per second. A comparison of the observed and calculated values is given in Table IX.

Within an accuracy of 3% the equations show good agreement between the observed and calculated velocity constants.

A comparison of the collision frequency Z with Z_A the Arrhenius constant ($\ln Z_A$ being equal to

TABLE IX

IODO PHENOL BLUE

Temp., °C.	$k_{\text{obsd.}}$ ($\times 10^4$)	$k_{\text{calcd.}}$ ($\times 10^4$)	$k_{\text{obsd.}} - k_{\text{calcd.}}$ ($\times 10^4$)	% diff.
20	1.16	1.16	0.00	0.0
25	1.64	1.64	.00	.0
30	2.30	2.30	.00	.0
BROM PHENOL BLUE				
20	2.45	2.44	0.01	0.4
25	3.48	3.47	.01	.3
30	4.94	4.81	.13	2.6
CHLOR PHENOL BLUE				
20	2.95	2.98	0.03	1.0
25	4.31	4.27	.04	1.0
30	6.02	6.06	.04	0.6

B in the above equation) gives the departure from normal behavior. This can be expressed by the factor P defined by the equation

$$P = Z_A/Z \qquad (9)$$

where Z is given by the equation

$$Z = \frac{N_0}{1000}\,\sigma_{1,2}\left\{8\pi kT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)\right\}^{1/2} \qquad (10)$$

N_0 is the Avogadro number, 6.06×10^{23}

$\sigma_{1,2}$ is the ionic radius of the reacting ions 1 and 2, the value taken as a fair approximation being 5.0×10^{-8} cm.

k is the gas constant, 8.315×10^7 ergs/deg./mole

M_1 is the molecular weight of the OH ion = 17

M_2 is the molecular weight of the divalent anion of brom phenol blue = 668

Substituting these values in equation (10) the value for the number of collisions Z per liter per gram molecule per second is 2.91×10^{11} at 20°.

The calculation results in a value of P of 9.04×10^{-7} for brom phenol blue reacting with hydroxyl ion at 20°. Moelwyn-Hughes[5] has recently given a theoretical equation for P in which the deviation from normal behavior is attributed to electrostatic forces. At zero ion concentration this equation is

$$P = e^{1/2}e^{-z_A z_B \epsilon^2 L/kDr} \qquad (11)$$

where z_A and z_B are the valences of the reacting ions, -1 and -2, respectively.

L is a constant for each liquid; for water it is 4.63×10^{-3}

D is the dielectric constant, 80.47 for water at 20°

k is the Boltzmann constant, 1.372×10^{-16} ergs/degree/mole.

ϵ is the electronic charge, 4.77×10^{-10} e. s. u.

r is the ionic radius in centimeters.

Substituting the values given above, r is found to be 1.37×10^{-8} cm., a value of the expected order of magnitude. As this value depends upon a P value calculated on the basis of $\sigma = 5 \times 10^{-8}$ cm., P was recalculated using the value of r from (11) and the process repeated until a constant value of P was obtained. For the three reactions the values of r are 1.48×10^{-8}, 1.61×10^{-8} and 1.68×10^{-8} cm. for iodo, brom and chlor phenol blue, respectively. The corresponding values of P are 4.3×10^{-6}, 12.7×10^{-6} and 19.5×10^{-6}.

Corresponding to equation (1) equation (12) gives the change of P with changing ionic strength and temperature

$$P = e^{1/2}e^{-z_A z_B \epsilon^2 L/kDr}\,e^{(z_A z_B \epsilon^2/2DkT)(3LT-1)\kappa} \qquad (12)$$

where $1/\kappa$ is the thickness of the ionic atmosphere. If we assume r to be constant the equation has the form

$$P = Ae^{(z_A z_B \epsilon^2/2DkT)(3LT-1)\kappa}$$

Evaluation of the exponential term containing κ shows that the term changes twenty-fivefold between zero and 0.2 ionic strength while the P calculated from the Arrhenius equation, on the assumption of a constant E_A, varies less than fourfold. The change of E_A with ionic strength is given by Moelwyn-Hughes by the equation

$$(E_A)\kappa_1 - (E_A)\kappa_2 = \frac{3}{2}\frac{N_0 z_A z_B \epsilon^2}{D} \times (LT-1)(\kappa_1-\kappa_2) \qquad (13)$$

According to this equation E_A should increase from $\mu = 0.001$ to 0.200 by 0.65 kcal. at 20°. An inspection of Tables VI, VII and VIII does not show such an increase.

The values of the energy of activation are not sufficiently accurate to test the effect of temperature on the energy of activation at different ionic strengths.

While equation (11) seems capable of accounting for extremely high and low values of P for reactions involving ions with charges of unlike and like sign, there are some cases in which this equation seems to yield negative values of r. Among such cases, found in Moelwyn-Hughes' "Kinetics of Reactions in Solution,"[6] are the reaction between chloroacetate ion and hydroxyl ion (p. 78) in which Z_A equals 4.55×10^{11}, and the reaction between iodoacetate ion and hydroxyl ion (p. 218) in which Z_A equals 6.3×10^{11}, the theoretical value for Z being given equal to 2.86×10^{11}.

Equation (12) would not be expected to hold over any appreciable range of ion concentration as it is derived from the Debye and Hückel equation for the electrostatic potential

$$\phi_A = (z_A \epsilon/Dr)e^{-\kappa r} \qquad (14)$$

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[5] Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A155**, 308 (1936).

[6] Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford University Press, 1933.

An equation corresponding to equation (2) can be derived from the equation

$$\phi_A = z_A\epsilon/[Da(1 + \kappa a)] \qquad (14')$$

where a is the average distance of closest approach of the centers of the ions. The resulting equation corresponding to equation (12) is

$$P = e^{1/2}\, e^{-z_Az_B\epsilon^2L/Dka} \times e^{(z_Az_B\epsilon^2/2DkT)[(3LT - 1)\kappa + 2a\kappa^2LT]/(1 + a\kappa)^2} \qquad (15)$$

The difference from (12) lies in the exponential term involving κ. Calculations show that P changes twelvefold between zero and 0.200 ionic strength. This equation also involves the assumption that E_A does not change with ionic strength.

Corresponding to equation (13) the use of (14′) yields a theoretical equation for the change of E_A with ionic concentration.

$$(E_A)_{\kappa_1} - (E_A)_{\kappa_2} = \frac{N_0z_Az_B\epsilon^2}{2D}(LT - 1) \times \left\{\frac{\kappa_1(3 + 2a\kappa_1)}{(1 + a\kappa_1)^2} - \frac{\kappa_2(3 + 2a\kappa_2)}{(1 + a\kappa_2)^2}\right. \qquad (16)$$

This equation predicts that E_A should increase by 0.45 kcal. from $\mu = 0.001$ to 0.200. The experiments reported in this paper are not in agreement with (13) or (16).

Summary

A kinetic study of the fading of chlor phenol blue, brom phenol blue and iodo phenol blue shows that the rate-determining step involves a reaction between the divalent anion of the sulfonphthalein and the hydroxyl ion.

The effects of ionic strength and temperature have been compared with the theory.

PHILADELPHIA, PENNA. RECEIVED JUNE 21, 1937

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Dissociation Constants of Chlor Phenol Blue and Iodo Phenol Blue[1]

BY FRANK W. PANEPINTO AND MARTIN KILPATRICK

In connection with the study of these indicators[1a] the dissociation constants were determined. The experimental method was that used by Kilpatrick[2] in determining the dissociation constant of brom phenol blue. The ratios of the dissociation constant of the indicators and suitable weak acids were determined colorimetrically at low ionic concentrations. Extrapolation to zero ion concentration was made in accordance with the equations

$$\log Kc(\text{Ind})/Kc(\text{acid}) = \log Ka(\text{Ind})/Ka(\text{acid}) + 1.0\sqrt{\mu} \qquad (1)$$

and

$$\log Kc(\text{Ind})/Kc(\text{acid}) = \log Ka(\text{Ind})/Ka(\text{acid}) + 1.0\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (2)$$

Tables I and II summarize the results with benzoate–benzoic acid buffers.

The extrapolation in accordance with equations (1) and (2) yields the ratios of the dissociation constants of the indicators.

The ratios of the thermodynamic dissociation constants of chlor phenol blue and iodo phenol blue to that of benzoic acid are 0.60 and 1.06,

TABLE I

THE DISSOCIATION CONSTANTS WITH BENZOATE BUFFERS

Indicator Concentration 2×10^{-5} *M*. Temp. 25 ± 1°

μ	0.02008	0.01008	0.00507	0.00257
$\frac{C(\text{Benzoic acid})}{C(\text{Benzoate})}$	0.991	0.985	0.978	0.945
Chlor phenol blue				
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	.821	.757	.722	.719
Iodo phenol blue				
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	1.35 1.33	1.32 1.31	1.27 1.27	1.26 1.24
$\frac{Kc(\text{CPB})}{Kc(\text{HB})}$	0.814	0.746	0.706	0.679
$\frac{Kc(\text{IPB})}{Kc(\text{HB})}$	1.34 1.32	1.30 1.29	1.23 1.23	1.19 1.17
$Kc(\text{HB}) \times 10^5$	8.41	7.71	7.41	7.04
$Kc(\text{CPB}) \times 10^5$	6.84	5.81	5.23	4.83
$Kc(\text{IPB}) \times 10^5$	11.3 11.1	10.0 9.9	9.1 9.1	8.4 8.2

TABLE II

THE DISSOCIATION CONSTANT OF CHLOR PHENOL BLUE WITH BENZOATE–BENZOIC ACID BUFFER

μ	0.00917	0.00757	0.00507	0.00339	0.00257
$\frac{C(\text{Benzoic acid})}{C(\text{Benzoate})}$	0.983	0.980	0.971	0.961	0.946
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	.738	.734	.721	.717	.709
$\frac{Kc(\text{CPB})}{Kc(\text{HB})}$	.731	.719	.700	.688	.671
$Kc(\text{HB}) \times 10^5$	7.68	7.60	7.41	7.10	7.04
$Kc(\text{CPB}) \times 10^5$	5.66	5.46	5.19	4.88	4.72

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[1] Abstracted from the dissertation of Frank W. Panepinto presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1937.

[1a] Panepinto and Kilpatrick, THIS JOURNAL, **59**, 1871 (1937).

[2] Kilpatrick, *ibid.*, **56**, 2048 (1934).