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Summary

1. The four straight chain octanols and the eighteen methylheptanols have been prepared in large experimental quantities by well-characterized synthetic methods. Six of the methylheptanols had not previously been made.

2. These 22 alcohols have been carefully purified by distillation through high-precision stills.

3. We and our collaborators in this Laboratory and other laboratories have determined, by actual measurement and mathematical derivation, a large number of physical and chemical properties of these alcohols. In general, each measured property was obtained for all the octanols by a single investigator over a short period of time using the same apparatus and technique.

4. Most of the data obtained in this Laboratory and some of those obtained elsewhere are brought together in tables arranged according to different positions of the hydroxyl group. As a rule, this variation causes the greatest change in properties.

5. The data have been plotted so as to show the variation in properties with changes of structure. The graphs have been grouped so as to show which properties change in the same direction and which inversely when the hydroxyl is moved.

6. The relations of the values obtained in this Laboratory to molecular structure have been discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rate and Equilibrium Studies of Carbinol Formation in the Triphenylmethane and Sulfonphthalein Dyes

BY SEYMORE HOCHBERG AND VICTOR K. LAMER

The determination of the effects of substituents and of molecular structure upon the rates of chemical reactions is a problem of interest and importance. The necessary measurements can be made most accurately and conveniently in aqueous media. Reactions involving dyestuffs are particularly well suited for such investigations but as is the case for most reactions in aqueous solution, the reactant species are frequently of an ionic nature. To analyze accurately the effects of substitution it is imperative that all disturbing influences arising from the presence of the net charges of the reactant molecules be eliminated or adequately corrected.

Even if the comparisons of different substituents are restricted to ionic reactions of the same electric charge type and ionic strength, it is possible that the comparisons may still be complicated by specific electrostatic effects which depend on the size of the reactant ions and the location of the charges in these molecules. These specific effects can be eliminated if a satisfactory method can be developed for correcting the rates of ionic reactions to the hypothetical rate for the corresponding uncharged reactants.

A well-recognized procedure is to determine the functional dependence of the free energy of activation ($-RT \ln k/\nu$) upon the dielectric constant of the medium at a given temperature and to extrapolate the results to infinite dielectric constant where all electrostatic effects vanish.

An alternate method has been presented by one of us.[1-3] It consists essentially in determining the rate of reaction in mixed solvents so chosen that the temperature coefficients of the rate may be evaluated not only under the customary re-

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[1] LaMer, *J. Franklin Inst.*, **225**, 709 (1938).

[2] Amis and LaMer, THIS JOURNAL, **61**, 905 (1939).

[3] Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

striction of constant composition but also under the restriction that the dielectric constant is held constant while the temperature is varied. Under the latter restriction, the electrostatic contribution to the entropy of activation vanishes, permitting a determination of the entropy of activation for the hypothetical reaction between the uncharged species directly from the experimental data.

The dyes containing the triphenylmethane nucleus react with hydroxyl ion to produce carbinols which are usually colorless compounds. In general the reaction comes to equilibrium. The fraction of colored form present at any time, t, can be determined accurately and conveniently with a colorimeter provided that the rate is not too rapid. The reaction for the sulfonphthalein dyes may be formulated as

$$R^{=} + OH^{-} \underset{k_2}{\overset{k_1}{\rightleftarrows}} ROH^{\equiv} \qquad (1)$$

$R^{=}$ is the colored form of the dye, k_1 is the molar rate constant for the forward reaction, and k_2 the corresponding constant for the reverse reaction. At equilibrium

$$\frac{(ROH^{\equiv})}{(R^{=})(OH^{-})} = \frac{k_1}{k_2} = K \qquad (2)$$

K is the equilibrium constant in volume molar concentrations.

The dependence of the reaction rate upon temperature is governed by the equation

$$k = \alpha e^{-\Delta E^*/RT} = \nu e^{-\Delta F^*/RT} \qquad (3)$$

$$\log_{10} k = B - \Delta E^*/2.3RT \qquad (4)$$

where ν is a frequency and ΔE^* and ΔF^* are the energy and free energy of activation. In the language of the collision theory the frequency factor α ($B = \log_{10}\alpha$) represents the molar frequency of favorable collisions. It is often set equal to PZ^0 where P is the so-called "steric" or "probability" factor of the British School and Z^0 is the gas kinetic collision frequency for the reactant molecules.

In the language of the "transition state" theory the quantity $(RT/Nh)e^{\Delta S^*/R}$ is equivalent to α. Here ΔS^* is the increase of entropy for the activation process including all degrees of freedom; h is Planck's constant; N is Avogadro's number; and R and T have their usual significance.[4,5]

Obviously differences in the rates of reaction may arise independently or concomitantly from differences in the energy of activation or from differences in the entropy of activation ΔS^* which, in turn, may be represented as differences in P. In this investigation we shall be interested in determining how substitution in the resonating nucleus of the dye affects these factors of equation (4).

The constants in Table I show that although the rate of carbinol formation is decreased by increasing the negative charge of the triphenylmethane ion in accord with the elementary principle that, other factors being equal, reactions between ions of opposite sign should be more rapid while those between ions of the same sign should be slower, the differences between the charge types are not as large as might be expected. Furthermore, the differences arising from variation of substituents within a given charge type are of the same order as the differences between dyes of different charge types. Table II shows that reactions of different charge type may have comparable rates through the compensation of the energy of activation by an entropy of activation of appropriate magnitude.

TABLE I

FIRST ORDER RATE CONSTANTS k (SEC.$^{-1}$) FOR THE RATE OF CARBINOL FORMATION OF DYES AT 25°

Ionic strength = 0.1 for all dyes of charge type −2; lower for others.

Dye	Abbr.	Charge	k
Brilliant green[a]	BG	+1	2.0
Malachite green[a]	MG	+1	1.8
Crystal violet[b]	CV	+1	0.22
Phenolphthalein[b]	PP	−2	.01
Dinitrophenol-sulfonphthalein	DNP	−2	.016
Brom phenol blue[c]	BPB	−2	.00090
Chlor phenol blue[c]	CPB	−2	.00078
Iodo phenol blue[c]	IPB	−2	.00030
Brom phenol red	BPR	−2	.000102
Brom cresol purple	BCP	−2	.0000171
Phenol red	PR	−2	.0000125
Brom cresol green	BCG	−2	.00000714
Brom thymol blue	BTB	−2	.000002

[a] Calculated from data of Sidgwick and Moore, ref. 8.
[b] Calculated from data of Biddle and Porter, ref. 12.
[c] Calculated from data of Panepinto and Kilpatrick, ref. 22. The constant of these authors is not in agreement with that of Amis and LaMer for BPB (0.00070) but is given for purposes of comparison with IPB and CPB.

Of the many dyestuffs, we have selected for intensive study several whose equilibrium constants and reaction rates in carbinol formation could be conveniently studied over a suitable range of temperature and dielectric constant.

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(4) LaMer and Kamner, THIS JOURNAL, **57**, 2662, 2669 (1935).

(5) Liotta and LaMer, *ibid.*, **60**, 1967 (1938).

TABLE II

THE FACTORS DETERMINING THE RATES OF TWO COMPARABLE REACTIONS OF DIFFERENT CHARGE TYPES[a,b]

Reaction	$k^{25°}_{K = 0}$ (sec.$^{-1}$)	ΔE^*	B	P	$r_A + r_B$, Å.
Hg^{++} + $Co(NH_3)_5Br^{++}$	1.21	12,300	8.11	4.3×10^{-4}	1.4
OH^- + $Co(NH_3)_5Br^{++}$	7.29	33,600	18.21	1.4×10^{6}	5.6

[a] Data—Brönsted and Livingston, THIS JOURNAL, 49, 435 (1927); [b] Calculations of $r_A + r_B$ (Å. units) by Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A155**, 308 (1936).

The carbinol formation of crystal violet has been investigated[6] by following the decrease of electrical conductance of an equimolecular mixture of crystal violet chloride and sodium hydroxide. Due to the apparent uncertainties in the reported kinetic results[6–8] we have reinvestigated the rate of formation of crystal violet carbinol by a conductance method.

Experimental Method

Conductimetric

Crystal Violet.—The National Aniline and Chemical Company's product was freed from zinc by precipitation of the carbinol with an excess of concentrated sodium hydroxide and solution in hydrochloric acid. This process was repeated until the supernatant liquid showed no test for zinc with hydrogen sulfide. The carbinol was dissolved in dilute hydrochloric acid, and recrystallized twice from water as the chloride. The crystals showed no flame test for sodium and a minute residue (less than one part per thousand), probably iron, on ashing. Five grams of the dye was dried at 80° until a weight loss of less than one part per thousand was detected after twenty-four hours in the oven at 80°. The cell constant of the conductance cell was 0.3648.

Conductance Bridge.—A Leeds and Northrup Slide Wire Bridge, a variable air condenser of 0.0014 mfd. and microphone hummer were used in conjunction with a standard resistance box. The balance point was detected with a loudspeaker after amplification. Measurements of resistance were precise to one part in five thousand.

The specific conductance of the water was 1×10^{-6} ohms^{-1} cm.$^{-1}$. The molar conductance for the chloride of crystal violet at 25° and 0.002 M was 99.5. Subtracting the conductance of the chloride ion (73.0) and adding the conductance of the hydroxyl ion (186.0) the molar conductance of the ionized crystal violet hydroxide becomes 212.5.

For three experiments 10 cc. of crystal violet 0.00998 M and 10 cc. of water were added by pipet to the conductance cell in a thermostat at 25 ± 0.005°. After thirty minutes, 10 cc. of 0.00998 M carbonate-free sodium hydroxide was added by volumetric pipet, the solution shaken and the readings of conductance were taken immediately. The pipet drained in ten seconds.

For five experiments a two-compartment reaction flask was used. After thirty minutes in the thermostat the flask was shaken and measurement of the time was started. The solution was then poured into the conductance cell. Two experiments were made at higher concentrations to check the bimolecular mechanism.

Calculation of the Rate Constant.—The reaction between the crystal violet cation and hydroxyl ion is of the type $R^+ + OH^- \rightarrow ROH$ (un-ionized).

For a second order reaction with equal concentrations of dye and hydroxyl ion the molar rate constant k can be calculated from the measured resistances as a function of the time through the equation

$$k = \frac{1}{t_2 - t_1}\left(\frac{\Lambda_{R^+} + \Lambda_{OH^-}}{1000\kappa}\right)\left(\frac{1}{\frac{1}{R_2} - \left(\frac{1}{R}\right)_{res}} - \frac{1}{\frac{1}{R_1} - \left(\frac{1}{R}\right)_{res}}\right) \quad (5)$$

κ is the cell constant, Λ is the equivalent conductance, R_1 and R_2 are the resistances at time t_1 and t_2 and $(1/R)_{res}$ is the conductance arising from the presence of Na^+ and Cl^- whose concentration does not change during the progress of the reaction. Since the ionic strength decreases with the progress of the reaction the molar conductances increase very slightly. This effect has been corrected for by using progressively increasing values of the conductances as computed from the Onsager equation.

$1/R - (1/R)_{res}$ is plotted as ordinate *vs.* t yielding the slope s.

$$s = \Delta\left(\frac{1}{\frac{1}{R} - \left(\frac{1}{R}\right)_{res}}\right) \Big/ \Delta t \quad (6)$$

and

$$k = s\left(\frac{\Lambda_{R^+} + \Lambda_{OH^-}}{1000K}\right) \quad (7)$$

Table III is abridged from a typical experiment in which 75 values of the conductance were read throughout the course of the reaction. The results are plotted in Fig. 1, along with a similar typical experiment at a higher concentration.

The observed value for the conductance of crystal violet hydroxide extrapolated to initial time is 200 in satisfactory agreement with the calculated value (207) referred to the same ionic strength by the Onsager equation.

Colorimetric

Sodium Hydroxide.—Eimer and Amend C. P. grade was treated to remove carbonate, made up to a concentration of approximately 1 M and stored in a paraffin-lined

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[6] Hantzsch and Osswald, *Ber.*, **33**, 278 (1900).

[7] Gerlinger, *ibid.*, **37**, 3958 (1904).

[8] See also Sidgwick and Moore, *J. Chem. Soc.*, **95**, 889 (1909), on brilliant green.

TABLE III

DATA FROM A TYPICAL CONDUCTANCE EXPERIMENT

Experiment 12.—Crystal Violet, NaOH 0.00332 *M*, 25.007°

Time, sec.	$(1/R) \times 10^3$, ohms^{-1}	$\dfrac{1}{\frac{1}{R} - \left(\frac{1}{R}\right)_{\text{res}}}$
30	2.853	567
240	2.490	719
405	2.320	820
540	2.224	891
750	2.107	996
1140	1.950	1182
1500	1.844	1357
1980	1.738	1585
2410	1.666	1792
3660	1.528	2387
4500	1.468	2796
6120	1.393	3546
	$k = 0.282$	

bottle. The sodium hydroxide was titrated differentially against sulfuric acid to determine the residual carbonate and was standardized against Bureau of Standards potassium acid phthalate.

Sulfonphthaleins.—Brom cresol purple, brom cresol green, phenol red and brom thymol blue, were LaMotte products; brom phenol red and dinitrophenolsulfonphthalein were from Hynson, Westcott and Dunning. Stock solutions were prepared as 2×10^{-4} *M* in distilled water and stored at 3° to prevent the growth of microörganisms.

Methanol.—Synthetic C. P. methanol was treated with sodium, silver nitrate and finally with magnesium turnings. After fractional distillation the density was 0.7868 g./cc. at 24.8° corresponding to 99.93% methanol.

Preparation of Kinetic Runs.—Amounts of methanol calculated from Åkerlöf's[9] data to yield mixtures of the proper dielectric constant (accurate to 0.14% equivalent to 1% in reaction rate constant) and sodium hydroxide were added from burets to a 250-cc. volumetric flask to make the final solution 0.1000 *M* in sodium hydroxide at the temperature of the experiment. The initial concentration of the dye was 2×10^{-5} *M* in all cases except for dinitrophenolsulfonphthalein where 6×10^{-5} *M* solution was used. For experiments at 25 and 35° paraffin-lined bottles were employed; Non-sol bottles at 45°.

Standard solutions of the dyes were prepared by adding 3 cc. of the stock solution from a hypodermic syringe to the proper amounts of the other components, such that the concentrations of sodium hydroxide and methanol in the standard were the same as in the solution to be measured. For experiments at 25° the time of injection of the dye to make up each standard used for comparison with reaction mixture was taken to determine the elapsed time of the reaction. At 35 and 45°, aliquots were pipetted from the reaction bottles to 50-cc. Erlenmeyer flasks and chilled to approximately 10°. Standards for these reactions were also chilled when prepared. The time of chilling of the sample for analysis was taken to determine the elapsed time of the experiment. For the experiments here described any time errors involved in the preparation of the standards are negligible.

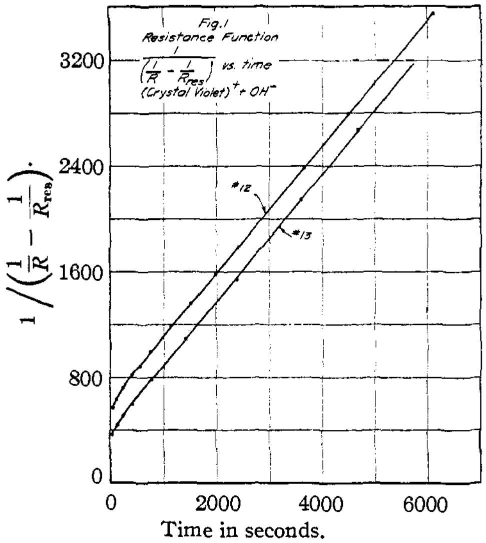

Fig. 1.—Resistance function $1 \Big/ \left(\frac{1}{R} - \frac{1}{R_{\text{res}}}\right)$ *vs.* time (crystal violet)$^+$ + OH$^-$.

Use of the Colorimeter.—Aliquots were compared with the standards in a Klett–Beaver colorimeter especially rebuilt[10] so that the length of the light path through the solvent and the number of glass-air and glass-water interfaces were identical on both sides of the colorimeter.

In making a comparison, the lower cups were filled with distilled water while the upper cups were filled with standard and unknown, respectively. The unknown was set so that the length of the light path through it was always 30 mm. The intensities were matched by adjusting the setting of the standard. After ten readings were taken the cups were emptied, rinsed and refilled with the standard and the unknown (positions reversed) and ten more readings were taken. The twenty readings were averaged to obtain the concentration of the colored form of the dye. This procedure eliminates errors due to differences in illumination of standard and unknown, inequalities in light transmission in both halves of the colorimeter and possible differences in sensitivity of different parts of the retina. Filters were introduced into the eyepiece to increase the precision of matching: Wratten no. 58 (green) for PR, BPR, BCP and Dinitrophenolsulfonphthalein; Wratten no. 23A (red) for BCG and BTB.

Approximately five determinations of concentration were made for each of the duplicate kinetic runs. The temperature was maintained constant to 0.005° and checked against a Bureau of Standards platinum resistance thermometer.

Method of Calculation of Colorimetric Constant.—When C is the concentration of the colored form of the dye at any time t and C_0 is its concentration when $t = 0$, the kinetic expression for Eq. (1) when a large excess of OH$^-$ is used (so that its concentration remains sensibly con-

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[9] Åkerlöf, THIS JOURNAL, 54, 4125 (1932).

[10] According to specifications of Amis and LaMer based on an unpublished critical study of the sources of error inherent in the customary colorimetric techniques with commercial colorimeters.

stant through the course of the reaction) becomes

$$k_1 = \frac{-2.303}{t\left(1 + \frac{1}{(\mathrm{OH}^-)K}\right)(\mathrm{OH}^-)} \log_{10}\left\{\frac{C}{C_0}\left(1 + \frac{1}{(\mathrm{OH}^-)K}\right) - \frac{1}{(\mathrm{OH}^-)K}\right\} \quad (8)$$

C/C_0 is obtained by dividing the colorimeter reading at time t by the calculated initial reading.

For purposes of calculation the following substitutions are made

$$K' = \frac{1}{K(\mathrm{OH})} \text{ and } k_1' = k(\mathrm{OH}^-) \quad (9)$$

For most runs K was determined approximately by the colorimeter reading near equilibrium and finally adjusted so that the calculated value of k_1 remained essentially constant throughout the run. This was necessary because of the length of time required for equilibrium. The selection of the final value of K has little effect on the average of k_1 for the run.

For the more rapid runs—for all dyes at 45° and for BPR at all temperatures—K was determined by waiting for the attainment of equilibrium. When the colorimeter reading at equilibrium is C_e, K' is given by

$$K' = \frac{C_e}{C_0 - C_e} \quad (10)$$

Table IV contains data from a typical colorimetric experiment.

TABLE IV

DATA FROM A TYPICAL COLORIMETRIC EXPERIMENT

Brom Cresol Purple, 0.100 M NaOH, 45°

Time, hr.	Colorimeter reading	C/C_0	k_1 (hr.$^{-1}$)
0.00	28.0	1.00	...
7.36	23.84	0.8513	0.260
8.68	22.82	.8149	.298
9.62	22.76	.8128	.274
25.62	19.31	.6896	.275
168.0	17.93	Used to determine K	
528.0	17.85[a]	Used to determine K	

[a] From this and a duplicate experiment 17.87 is taken as the equilibrium reading and K' = 1.76. Values of k_1 are calculated using equations (16) and (15).

Results

Conductimetric Measurements.—Conductimetric rate measurements of the carbinol formation of crystal violet yielded values of k for eight experiments of 0.284 (sec.$^{-1}$; av. dev. ±0.004) when the initial ionic concentration is 0.0066 M and 0.270 (av. dev. ±0.002) for two experiments with initial ionic concentration of 0.01 M. The reliability of the measurements is only *ca.* 5% since it involves a calculated value for the conductance of ionized crystal violet hydroxide.

Colorimetric Experiments.—The approximate rates of carbinol formation in 0.100 M sodium hydroxide were determined for certain sulfonphthaleins for purposes of orientation. These, together with other pertinent data, are given in Table I.

Data for the dyes selected for intensive study are given in Table V. The reliability of the rate constants is about 2%. The equilibrium constants are reliable to about 3% for BCP, 5–10% for BPR and are only correct for order of magnitude for BCG. The precision of measurement of the rate constant of carbinol formation depends upon the equilibrium constant of the reaction. For this reason, kinetic data for experiments with small equilibrium constants (BCP at 45°, BCP at 25° and D = 66.79) are less reliable (*ca.* 4%) than those with larger equilibrium constants.

TABLE V

RATE CONSTANTS k_1 (IN SEC.$^{-1}$ MOLE^{-1}) AND EQUILIBRIUM CONSTANTS K FOR CARBINOL FORMATION IN THE SULFONPHTHALEIN SERIES

NaOH, 0.1000 M, water–methanol

	25°		35°		45°	
D	$k_1 \times 10^5$	K	$k_1 \times 10^5$	K	$k_1 \times 10^5$	K
Brom Phenol Red, $r_A + r_B$ = 1.33 Å.						
78.54	10.17	77				
75.12	7.03	56				
74.87	....	....	21.17	50		
71.42	4.39	50	14.31	42	42.42	34
Brom Cresol Purple, $r_A + r_B$ = 1.21 Å.						
78.54	1.705	15.15				
75.12	1.117	10.87				
74.87	....	....	3.57	9.43		
71.42	0.667	8.00	2.364	6.90	7.72	5.68
66.79	0.331	4.55				
Brom Cresol Green, $r_A + r_B$ = 1.24 Å.						
78.54	0.714	500				
75.12	.4734	300				
74.87	....	....	1.825	300		
71.42	.2856	200	1.214	200	4.364	200

Discussion of Results

Conductimetric Measurements.—From Fig. 1 it is evident that after a brief induction period the data for the fading of crystal violet are linear, corresponding to a second order reaction and to the proposed mechanism. Increasing the initial concentration from 0.00666 to 0.00998 M reduces the rate constant by 5%. For a positive ion reacting with a negative ion, both singly charged, this primary salt effect[11] should be 4%. The difference is within the experimental error.

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[11] (a) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); (b) LaMer, *Chem. Rev.*, **10**, 179 (1932).

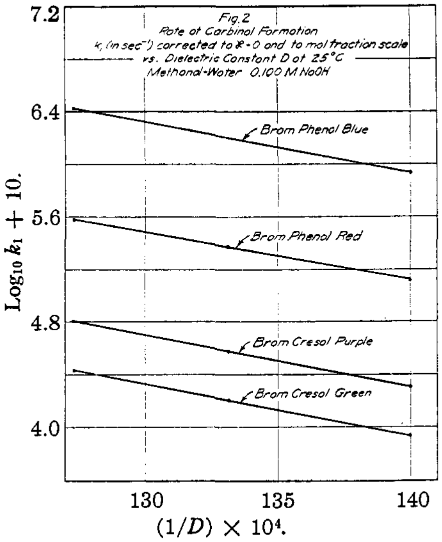

Fig. 2.—Rate of carbinol formation, k_1 (in sec.$^{-1}$) corrected to K = 0 and to mole fraction scale *vs.* dielectric constant D at 25°; methanol–water, 0.100 M NaOH.

Our conductimetric rate constant for crystal violet is 27% larger than the colorimetric rate constant of Biddle and Porter,[12] who employed an excess of hydroxide to make the reaction first order. Inasmuch as the half time of the reaction is about fifteen minutes, a more accurate measurement by a visual colorimetric technique cannot be expected.

Colorimetric Measurements

The Equilibrium Constant.—The equilibrium constant for an ionic reaction depends not only upon the temperature but upon the dielectric constant as well. The special case of the ionization constants of acids has been discussed recently.[13–16] LaMer and Brescia point out the convenience of evaluating such equilibrium constants in isodielectric media as well as in media of constant composition.

The equilibrium constants given in Table V and Figs. 3 and 4 are the stoichiometric quantities K_c rather than the thermodynamic ones K_a ($= K_cK_f$). The heat evolved ($-\Delta H^0$), when initial and final species are in the standard state of unit activity, is related to the equilibrium constants by the sum of two terms.

$$-\Delta H^0 = R\frac{\mathrm{d}\ln K_a}{\mathrm{d}1/T} = R\left(\frac{\mathrm{d}\ln K_c}{\mathrm{d}1/T}\right) + R\left(\frac{\mathrm{d}\ln K_f}{\mathrm{d}1/T}\right) \qquad (11)$$

The first one involving K_c may be taken from Fig. 3 and the second involving K_f is calculated from electrostatic theory.

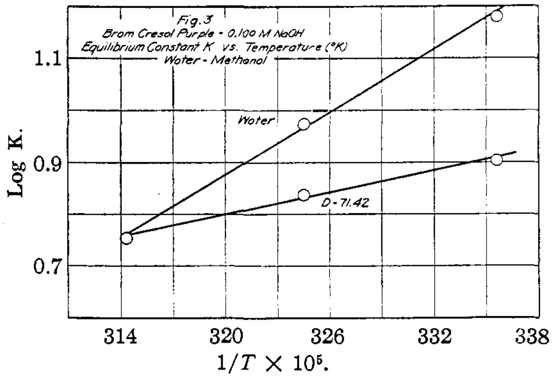

Fig. 3.—Brom cresol purple—0.100 M NaOH: equilibrium constant K *vs.* temperature (°K.); water–methanol.

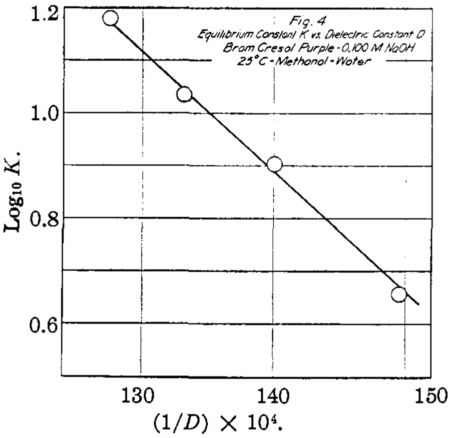

Fig. 4.—Equilibrium constant K *vs.* dielectric constant D; brom cresol purple—0.100 M NaOH; 25°, methanol–water.

For a reversible reaction involving the ions A and B and its carbinol, R

$$A^{Z_A} + B^{Z_B} \rightleftarrows R^{Z_A+Z_B} \qquad (12)$$

$$K_f = \frac{f_{Z_A+Z_B}}{f_{Z_A}f_{Z_B}} \qquad (13)$$

where the symbol f_i refers to the activity coefficient for the particular ion i of algebraic charge number z_i.

$$\ln K_f = \ln f_{Z_A+Z_B} - \ln f_{Z_A} - \ln f_{Z_B} \qquad (14)$$

The activity coefficients of the ions may be determined from the Debye–Hückel[17] first approximation.

$$-\ln f_i = \frac{Z_i^2\epsilon^2\kappa}{2DkT(1 + a\kappa)} \qquad (15)$$

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(12) Biddle and Porter, THIS JOURNAL, **37**, 1571 (1915).

(13) Baughan, *J. Chem. Phys.*, **7**, 951 (1939).

(14) Gurney, *ibid.*, **6**, 499 (1938).

(15) Minnick and Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939); Elliott and Kilpatrick, *ibid.*, **45**, 454–492 (1941).

(16) LaMer and Brescia, THIS JOURNAL, **62**, 617 (1940).

(17) See ref. 11b.

where κ is related to the ionic strength μ by the relation

$$\kappa = \sqrt{\frac{8\pi\epsilon^2N}{1000DkT}}\sqrt{\mu} \qquad (16)$$

For media of constant composition (subscript C), an increase in temperature affects K_f by changing both T and D of equation 15 as follows

$$\left[\frac{-\Delta H^0}{R}\right]_C = \left[\frac{\mathrm{d}\ln K_c}{\mathrm{d}1/T}\right]_C + \left[\frac{\partial \ln K_f}{\partial 1/T}\right]_D + \left[\frac{\partial \ln K_f}{\partial 1/D}\right]_T \frac{\mathrm{d}1/D}{\mathrm{d}1/T} \qquad (17)$$

On the other hand, for media of constant D (Subscript D) K_f is dependent only upon the temperature and

$$\left[\frac{-\Delta H^0}{R}\right]_D = \left[\frac{\mathrm{d}\ln K_c}{\mathrm{d}1/T}\right]_D + \left[\frac{\partial \ln K_f}{\partial 1/T}\right]_D \qquad (18)$$

Using equations 14 and 15 and noting that κ is a function of T and D, the differentiations indicated in equations 17 and 18 yield the equations

$$\left[\frac{-\Delta H^0}{R}\right]_C = \left[\frac{\mathrm{d}\ln K_c}{\mathrm{d}1/T}\right]_C - \left[1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right] Z_AZ_B\left[\frac{\epsilon^2\kappa}{kD(1+a\kappa)} + \frac{\epsilon^2\kappa}{2kD(1+a\kappa)^2}\right] \qquad (19)$$

$$\left[\frac{-\Delta H^0}{R}\right]_D = \left[\frac{\mathrm{d}\ln K_c}{\mathrm{d}1/T}\right]_D - Z_AZ_B\left[\frac{\epsilon^2\kappa}{kD(1+a\kappa)} + \frac{\epsilon^2\kappa}{2kD(1+a\kappa)^2}\right] \qquad (20)$$

Substituting the value[18] $a = 5$ Å., d ln D/d ln T = -1.455, and inserting the values of d ln K_c/d $1/T$ from Fig. 3 yields

$$\Delta H^0_D = -2000 \text{ cal./mole} \qquad (21)$$

$$\Delta H^0_C = -9600 \text{ cal./mole} \qquad (22)$$

$$\Delta H^0_C - \Delta H^0_D = -7600 \text{ cal./mole} \qquad (23)$$

For an ideal non-ionic reaction this difference in heats of reaction would not exist. The deviation of the present reaction from the ideal is to be ascribed to the energy relations involved in the work of charging the ions in the different media.

The partial free energy increase on charging one mole of ions of radius a to a charge $Z_A\epsilon$ in a medium of dielectric constant D is given by

$$\overline{F}_B = \frac{Z_A^2\epsilon^2N}{2Da} \qquad (24)$$

Subscript B indicates a Born term. For reaction 12

$$\Delta F^0_B = \frac{\epsilon^2N}{2D}\left\{\frac{(Z_A+Z_B)^2}{c} - \frac{Z_A^2}{a} - \frac{Z_B^2}{b}\right\} \qquad (25)$$

where c is the radius of the ion, R. If, as a first approximation, $a = b = c = r$, then

$$\Delta F^0_B = z_Az_B\epsilon^2N/Dr \qquad (26)$$

Now, since $\Delta F^0_B/T$ is a function of T and D

$$\Delta H^0_{BC} = \left[\frac{\mathrm{d}\,\frac{\Delta F^0_B}{T}}{\mathrm{d}\,\frac{1}{T}}\right]_C = \left[\frac{\partial\,\frac{\Delta F^0_B}{T}}{\partial\,1/T}\right]_D + \left[\frac{\partial\,\frac{\Delta F^0_B}{T}}{\partial\,1/D}\right]_T \frac{\mathrm{d}1/D}{\mathrm{d}1/T} \qquad (27)$$

and

$$\Delta H^0_{BD} = \left[\frac{\mathrm{d}\,\frac{\Delta F^0_B}{T}}{\mathrm{d}1/T}\right]_D \qquad (28)$$

Carrying out the indicated operations

$$\Delta H^0_{BD} = \Delta F^0_B \qquad (29)$$

$$\Delta H^0_{BC} = \Delta F^0_B\left(1 + \frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right) \qquad (30)$$

$$(\Delta H^0_C - \Delta H^0_D) = \Delta F^0_B\left(\frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right) = \frac{z_Az_B\epsilon^2N}{Dr}\left(\frac{\mathrm{d}\ln D}{\mathrm{d}\ln T}\right) \qquad (31)$$

Inserting the value of -7600 cal. for $(\Delta H^0_C - \Delta H^0_D)$ and -1.455 for d ln D/d ln T, the value of r calculated is 1.68 Å., or 1.62 Å. when a is taken as 3 Å. in the interionic attraction correction instead of 5 Å. This is not an unreasonable value for the ionic parameter. The electrostatic treatment given above therefore accounts for the thermodynamic behavior of these equilibria as functions of temperature and dielectric constant as far as the Born theory permits at the present time.

The Reverse Reaction.—The reverse reaction involves the decomposition of the triply charged carbinol. To establish the identity of the molecule reacting with the carbinol, it is necessary to vary its amount and to study the effect of its variation on the rate constant of the reverse reaction. Kober and Marshall[19] who investigated the reaction of phenolphthalein with hydroxyl ion in the presence of alcohol and other reagents concluded that the rate of the reverse reaction was directly proportional to the concentration of water. Bodforss and Leden,[20] however, concluded that the rate of the reverse reaction was independent of the concentration of water. Table VI gives values for k_2, the rate constant for the carbinol decomposition of BCP, which decrease with increasing methanol content. This decrease is too small to be due to any ionic reaction (such as $2\mathrm{ROH}^{=} \rightarrow 2\mathrm{R}^{-} + 2\mathrm{OH}^{-}$).

Our experiments with BPR are pertinent and those with BCP are competent to decide whether or not water is involved in the kinetic reaction.

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[18] See ref. 2, p. 911.

[19] Kober and Marshall, THIS JOURNAL, **33**, 59 (1911).

[20] Bodforss and Leden, *Z. anorg. allgem. Chem.*, **234**, 239 (1937).

TABLE VI

REVERSE REACTION RATE CONSTANTS k_2 (SEC.$^{-1}$)

$$\text{Carbinol}^{=} \xrightarrow{k_2} \text{Dye}^{-} + \text{OH}^{-}$$

	10^6k_2, BCP			10^6k_2, BPR		
D	25°	35°	45°	25°	35°	45°
78.54	1.125			1.32		
75.12	1.026			1.26		
74.87	...	3.78		..	4.23	
71.42	0.834	3.43	13.4	0.88	3.42	13.6
66.79	0.727					

H_2O + Carbinol$^{=}$ → Dye^{-} + OH^- + H_2O (see Table VII)

	10^6k_2/activity of water, BCP			10^6k_2/activity of water, BPR		
D	25°	35°	45°	25°	35°	45°
78.54	1.13			1.3		
75.12	1.21			1.5		
74.87	..	3.8		...	4.2	
71.42	1.06	3.9	13.4	1.1	3.9	13.6
66.79	1.06					

TABLE VII

ACTIVITY OF WATER[a] IN METHANOL–WATER SOLUTIONS USED WITH REFERENCE TO PURE WATER

T, °C.	D	A
25	78.54	1.00
25	75.12	0.85
25	74.87	.85
25	71.42	.79
25	66.79	.67
35	74.87	1.00
35	71.42	0.87
45	71.42	1.00

[a] Calculated from partial vapor pressures of methanol-water solutions. "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., Vol. III, p. 290.

The data in Table VI show that the rate of the reverse reaction is linearly proportional to the *activity* of water present. The observation of Bodforss and Leden is extraordinary since it would require the spontaneous decomposition of a single ion of the carbinol in the solution.

TABLE VIII

EFFECT OF SUBSTITUENTS ON RATE OF CARBINOL FORMATION (25°)

Substitution for H	To be compared No. 1	No. 2	$\log \frac{k_1\ (\text{No. 1})}{k_2\ (\text{No. 2})}$	μ^a	σ^b
$2NO_2$	DNP	PR	+3.1	−3.95	0.71
2Br	BPB[c]	BPR	+0.84	−1.52	.39
2Br	BPR	PR	+ .91	−1.52	.39
$2CH_3$	BCP	BPR	− .78	+0.4	− .07
$2CH_3$[d]	CR	PR	− .9	+0.4	− .07
4Br	BPB[c]	PR	+1.75	−1.52	.39
4Br[e]	BPB	PR	+1.85	−1.52	.39
4Cl[e]	CPB	PR	+1.79	−1.55	.37
4I[e]	IPB	PR	+1.38	−1.3	.35

[a] Dipole moment with respect to benzene ring for a single substituent—in Debye units. [b] For a single substituent as defined by Hammett, ref. 23, p. 186, and given in table on p. 188. [c] Amis and LaMer, ref. 2. [d] Thiel, *Monatsh.*, **53/54**, 1008 (1929); approximate. [e] Panepinto and Kilpatrick, ref. 22.

The Rates of Reaction. The Effects of Substitution.—The rate constants for the carbinol formation of the sulfonphthaleins given in Table I reveal that the substitution of negative groups on the chromophoric rings accelerates the reaction. In this reaction, as in several others, the "polar sequence"[21] of NO_2 > Hal > H > Alkyl appears to govern the rate of the reaction. A comparison of the dyes in Table VIII indicates that the succession of reaction rates is substantially in the same order as the dipole moments, the group having the largest negative dipole moment having the greatest influence on increasing the rate of the reaction. The data of Panepinto and Kilpatrick[22] show that the halogen substitutions are ordered as Br $\gtrsim$ Cl > I, which is not in conformity with the dipole moments which are ordered as Cl $\gtrsim$ Br > I. However, they are in the order predicted from Hammett's[23] Substituent Constants σ, derived from data on the dissociation constants of benzoic acid derivatives.

Ri and Eyring[24] ascribe the orienting effects of substituents in the nitration of benzene compounds to the effective charges residing on *o*-, *m*- and *p*-carbon atoms produced in turn by the dipole created by the presence of the substituent. The effective charge controls the electrical attraction of NO_2^+, which in turn influences the rate of reaction through the free energy of activation.

However, the free energy of activation comprises the entropy and energy of activation according to the relation

$$k = \nu e^{-\Delta F^*/RT} = \nu e^{\Delta S^*/R} e^{-\Delta E^*/RT} \qquad (32)$$

The effects of substituents should therefore be further analyzed to determine which of the two quantities is the dominating factor. In the chlorination of phenolic ethers,[25-27] the benzoylation of anilines,[28] the alkaline hydrolysis of benzoic esters[29,30] and the reaction of methyl iodide with dimethylanilines,[31] it has been observed that dif-

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(21) Watson, "Annual Reports, Chemical Society," 1938, Vol. XXXV, p. 236.

(22) Panepinto and Kilpatrick, THIS JOURNAL, **59**, 1871 (1937).

(23) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 188.

(24) Ri and Eyring, *J. Chem. Phys.*, **8**, 433 (1940).

(25) Bradfield and Jones, *J. Chem. Soc.*, 1006, 3073 (1928).

(26) Bradfield, Jones and Spencer, *ibid.*, 2907 (1931).

(27) Bradfield, *Chem. and Ind.*, **51**, 254 (1932).

(28) Williams and Hinshelwood, *J. Chem. Soc.*, 1079 (1934).

(29) Ingold and Nathan, *ibid.*, 222 (1936).

(30) Evans, Gordon and Watson, *ibid.*, 1430 (1937).

(31) Laidler, *ibid.*, 1786 (1938).

ferences in rate of reaction arise mainly from differences in the energy of activation rather than the entropy of activation, which remains constant. In all of these cases, as in the case of all of the sulphonphthaleins here investigated, except BCG and BTB, the substituent groups studied are relatively far from the reactive carbon atom—here the central carbon atom.

On the other hand, it has been found that a substituent situated close to the reactive position influences not only the energy but also the entropy of activation. This "proximity" or "ortho" effect has been observed for the esterification of aliphatic acids,[32] the addition of alkyl halides to tertiary bases,[33] and generally for reactions of *o*-substituted aromatic compounds.[34] BCG and BTB have methyl groups which are in close proximity to the reactive position. For further details on the effect of substituents the reader is referred to recent texts.[35,36]

However, the comparison of energies of activation of ionic reactions when determined in the customary manner (*i. e.*, in a medium of constant composition) is open to the objection that the comparison is affected not only by the character of the reacting molecules but also by changes in the solvent accompanying changes in temperature. It has been shown recently by one of us[37] that the situation becomes subject to a simple theoretical treatment when the comparisons of the entropies of activation are derived from rates of reaction in media of constant dielectric constant.

The effect of the solvent upon the reaction rate of an ionic reaction is given by the Christiansen–Scatchard equation.[38-40]

$$\log_{10} k = \log_{10} k_\infty - \frac{z_A z_B \epsilon^2 N}{2.3DRT}\frac{1}{r_A + r_B} + \frac{z_A z_B \epsilon^2 N}{2.3DRT}\frac{\kappa}{1 + a\kappa} \quad (33)$$

k_∞ is the molar rate constant extrapolated to a medium of infinite dielectric constant where all electrostatic effects vanish.

The second term of the right-hand member of equation 33 involves the decrease in log k due to the mutual repulsion of the electric charges z_A and z_B (of same sign) on the reactant molecules in a medium of finite dielectric constant. $r_A + r_B$ is the distance of approach of the centers of the reactant ions when reaction occurs. The last term of equation 33 is the contribution to the rate constant arising from the reduction of repulsive forces between the reactant ions due to the presence of an ionic atmosphere around each reactant ion.

It has been suggested[41] that the mole fraction rather than the molar concentration of reactants is the appropriate scale in the determination of rate constants. Therefore rate constants determined at constant molar concentration of reactants but in media of different molar volumes should be converted to rate constants at constant mole fraction before making comparisons.

This is accomplished by multiplying the rate constant extrapolated to zero ionic strength by a factor which is the ratio of the total moles per liter in the particular medium divided by the total moles per liter in the reference solvent (here taken as water at 25°).

The correction accounts for the specific solvent effects for the bromoacetate–thiosulfate reaction and the quenching of fluorescence.[42]

The conversion to the mole fraction scale is significant in the present case in isodielectric mixtures but is negligible in media of constant composition. In addition, it should be observed that this correction is identical for all the dyes.

Values of $r_A + r_B$ calculated from data corrected to mole fractions using equation 33 are given in Table V and should be compared with the value 1.25 Å. calculated from the data[2] for BPB.

The dependence of the rate constants on temperature is illustrated in Figs. 5, 6 and 7. After normalizing to infinite dilution and to a mole fraction basis values of ΔE^* and ΔS^* defined by the equations

$$\Delta E^*_{(\kappa=0)} = 2.3RT^2 \frac{\mathrm{d} \log k_{(\kappa=0)}}{\mathrm{d}T} \quad (34)$$

$$\Delta S^*_{(\kappa=0)} = 2.3R\left[\log k_{(\kappa=0)} - \log \frac{RT}{Nh} + \frac{\Delta E^*_{(\kappa=0)}}{2.3RT}\right] \quad (35)$$

can be corrected for the effect of the dielectric constant by decomposing the logarithm of the rate constant as follows

$$\log k_{(\kappa=0)} = \log k_\infty + \log k_B \quad (36)$$

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[32] Hinshelwood and Legard, *J. Chem. Soc.*, 587 (1935).

[33] Winkler and Hinshelwood, *ibid.*, 1147 (1935).

[34] See ref. 23, p. 204.

[35] See ref. 23 above, especially chap. 3 and 7.

[36] Glasstone, Laidler and Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

[37] See refs. 1, 2, 3 above.

[38] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

[39] Scatchard, *Chem. Rev.*, **10**, 229 (1932).

[40] Laidler and Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940); see pp. 316–323 and discussion by Scatchard, pp. 341–344.

[41] See ref. 40, p. 342.

[42] Unpublished work of H. G. Davis and V. K. LaMer.

where log k_B refers to the term

$$\frac{-z_A z_B \epsilon^2 N}{2.3DRT}\,\frac{1}{r_A + r_B}$$

of eq. 40.

Since log k_B may be written as constant/DT, $\Delta F_B^{\ddagger}$ ($= -RT \ln k_B$) may be written as constant'/D and its derivative with temperature in isodielectric solvents is zero. The entropy of activation for $\kappa = 0$ in isodielectric solvents is equal to the entropy of activation corrected for the charges of the ions.[1,2]

Table IX gives energies and entropies of activation for the several dyes. It will be observed that the entropies of activation for the *m*-substituted dyes are essentially the same while the energies of activation determine the rate constant. The effects of ΔE^* and ΔS^* are more readily compared in Table X where equal changes in the terms $\Delta S^*/2.3R$ and $\Delta E^*/2.3RT$ have equal effects on the reaction rate. On the other hand, the substitution of the methyl group in the *o*-position changes both the energy and the entropy of activation.

TABLE IX

ENERGIES OF ACTIVATION ΔE^* ($\kappa = 0$) AND ENTROPIES OF ACTIVATION ΔS^* ($\kappa = 0$) FOR THE RATE OF CARBINOL FORMATION OF VARIOUS SULFONPHTHALEINS DETERMINED BY TEMPERATURE COEFFICIENTS OF THE RATE AT 25, 35 AND 45°; ENERGY IN UNIT CALORIES

	Solvent water (const. comp.)		Isodielectric CH_3OH–H_2O solvents, $D = 71.42$	
Dye	ΔE^* ($\kappa = 0$)	ΔS^* ($\kappa = 0$)	ΔE^* ($\kappa = 0$)	ΔS^* ($\kappa = 0$)
BPB[a]	11,700	−35.6	22,300	−2.4
CPB[b]	11,600	−36	....	...
IPB[b]	11,820	−37	....	...
BPR	13,000	−35.2	23,100	−3.4
BCP	13,800	−36.0	24.800	−1.4
BCG	16,600	−28.3	27,400	+5.7

[a] Calculated from data of Amis and LaMer. [b] Calculated from data of Panepinto and Kilpatrick (25–35°).

TABLE X

ENERGIES AND ENTROPIES OF ACTIVATION FOR CONSTANT COMPOSITION AND CONSTANT DIELECTRIC CONSTANT (DATA AT 25°, $\kappa = 0$)

	Solvent, water, constant composition			Isodielectric solvent methanol–water, $D = 71.42$		
	log k + 10	$\frac{\Delta E^*}{2.3RT}$	$\frac{\Delta S^*}{2.3R}$	log k + 10	$\frac{\Delta E^*}{2.3RT}$	$\frac{\Delta S^*}{2.3R}$
BPB	6.42	8.57	−7.80	5.94	16.35	−0.52
BPR	5.58	9.53	−7.69	5.12	16.91	− .75
BCP	4.81	10.11	−7.88	4.30	18.20	− .30
BCG	4.43	12.18	−6.19	3.94	20.10	+1.24

Comparison with Collision Theory.—The gas collision frequency Z^0 can be computed from the mean collision diameter σ_{12} and the molecular weights of the reactants by the familiar equation of kinetic theory. Substituting for M_1 the molecular weight of hydroxyl ion (17.01) and for M_2 the different molecular weights of the dye ions gives an almost identical value

$$\log_{10} Z^0/\sigma_{12}^2 = 26.07 \qquad (37)$$

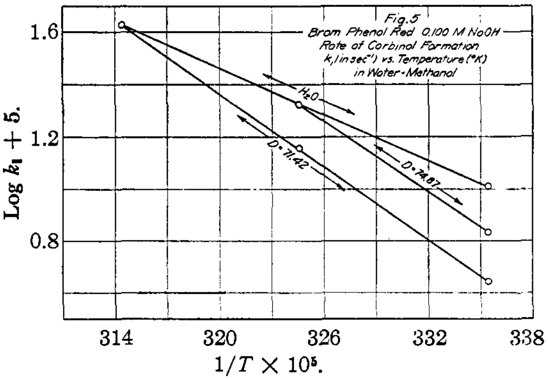

Fig. 5.—Brom phenol red 0.100 M NaOH: rate of carbinol formation, k_1 (in sec.$^{-1}$) *vs.* temperature (°K.) in water–methanol.

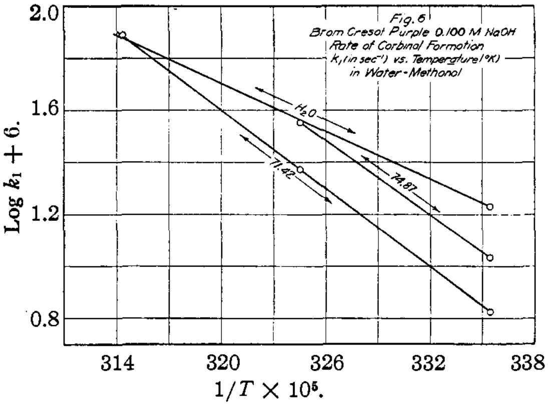

Fig. 6.—Brom cresol purple 0.100 M NaOH: rate of carbinol formation, k_1 (in sec.$^{-1}$) *vs.* temperature (°K.) in water–methanol.

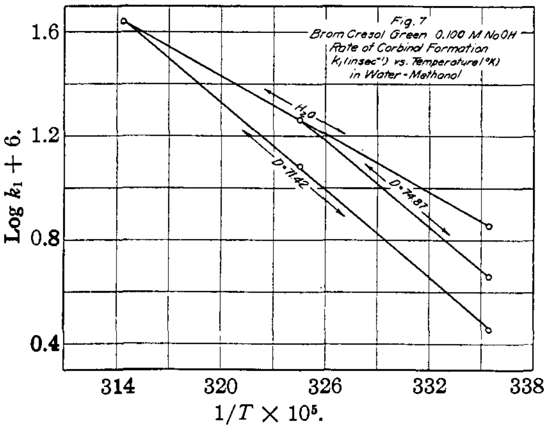

Fig. 7.—Brom cresol green 0.100 M NaOH: rate of carbinol formation, k_1 (in sec.$^{-1}$) *vs.* temperature (°K.) in water–methanol.

for BPB, BPR, BCP and BCG. Hence the collision theory would predict identical values of $\alpha = \log B$ for each dye since the radii $(r_A + r_B)$ from Fig. 2 and Table V are the same. This prediction is not in accord with the facts.

PZ^0 is related to the calculated thermodynamic quantities of Table IX by the relation

$$\log_{10} PZ^0 = \log_{10} \frac{RT}{Nh} + \frac{\Delta S_D^*(\kappa = 0)}{2.3R}$$

$$= 12.80 + \frac{\Delta S_D^*(\kappa = 0)}{2.3R} \qquad (38)$$

from (37) and (38)

$$\log_{10} P = \frac{\Delta S_D^*(\kappa = 0)}{2.3R} - \log \sigma_{12}^2 - 13.27 \qquad (39)$$

Assigning P the value 1, the values of σ_{12} of Table XI are obtained. On the other hand, arbitrary assignment of values to σ_{12} yields the values of P in the same table.

TABLE XI

VALUES OF σ_{12} (IN Å.) CALCULATED FOR $P = 1$ AND VALUES OF P CALCULATED FOR $\sigma_{12} = 3$ Å. AND 5 Å.

	σ_{12} $P = 1$	P, $\sigma_{12} = 3$ Å.	P, $\sigma_{12} = 5$ Å.
BPB	13	18	6
BPR	10	11	4
BCP	16	30	11
BCG	98	1050	370

In the "transition state" theory, the rate constant k may be written as

$$k = \frac{RT}{Nh} \frac{F^*}{F_A F_B} e^{-\Delta E_0/RT}$$

where ΔE_0 is the difference in zero point energies for the activated complex and initial reagents, respectively. F^*, F_A, F_B are the partition functions of the complex and reactants.

It has been shown that the introduction of the appropriate partition functions for a reaction involving only two atoms to form a double sphere complex reduces the transition state expression to that of the simple collision theory with $P = 1$.

When the simple collision theory (with $P = 1$) does not hold as is the case for more complex molecules the transition state theory attributes this to differences in vibrational and rotational levels of the reactant molecules and the activated complex which affect the ratio of the partition functions.

From the above treatment it seems clear that substituents particularly when they are in "ortho position" exercise their influence upon the entropy of activation through the vibrational and rotational partition functions rather than through the translational partition functions. The simple collision theory attributed all such effects to a collision diameter or steric factor.

Conclusions

1. The rate (k_1) and equilibrium (K) constants for the formation of the carbinols of the dyes, brom phenol red, brom cresol purple and brom cresol green have been measured in water and in isodielectric mixtures of water and methanol at 25, 35 and 45° and compared with previous data for brom phenol blue. Approximate rate constants were obtained for other sulfonphthaleins.

2. The bimolecular mechanism of carbinol formation based on colorimetric measurements has been verified for crystal violet by electrical conductance measurements.

3. The reverse reaction involving the decomposition of the carbinol to regenerate the colored form of the dye involves a molecule of water.

4. At constant T, $\log k_1$ is linearly dependent upon $1/D$, when the rates are normalized to the mole fraction scale.

5. The energy of activation and the frequency factor are constant over the range of temperature for the dyes studied.

6. The rates of reaction of *m*-substituted sulfonphthaleins are in the same order as the "substituent constant" derived for substituents on a benzene molecule.

7. For the *m*-substituted sulfonphthaleins the rate of the reaction is affected exclusively by changes in the energy of activation, the entropy of activation remaining constant.

8. Ortho substitution, in contrast to meta substitution, changes both the energy and the entropy of activation.

9. The dependence of the equilibrium constant upon T and D in media of constant composition and of constant dielectric constant has been analyzed on the basis of electrostatic theory.

10. The rates of carbinol formation for four sulfonphthaleins have been compared with the predictions of the collision theory.

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