The maximum CH_2 value is 17.4 units, or 59%, greater than the minimum. The average CH_2 value is 38.5 units. It is interesting to note that in no case below amyl in the regular symmetrical increase of the chains is the CH_2 value equal to that given by Mumford and Phillips.

Summary

1. The surface tensions and parachors of sixteen tertiary alcohols have been determined.

2. The parachors are found to increase with temperature in the order of approximately 0.2% per 10° rise in temperature.

3. The effect of substitution in trimethylcarbinol has been found to be most constitutive with the first CH_2 units added to the molecule, and to become more regular as the length of the carbon chains becomes greater.

4. Values for the CH_2 groups in tertiary alcohols have been determined which yield closer agreement between the calculated and observed parachors than the values previously used.

EMORY UNIVERSITY, GA.   RECEIVED JANUARY 9, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Entropies and Energies of Activation of Ionic Reactions.   The Kinetics of the Alkaline Fading of Brom Phenol Blue in Isodielectric Media

BY EDWARD S. AMIS AND VICTOR K. LA MER

The rates of many reactions between ionic species can be measured with a precision and ease exceeding that of non-ionic reactions. The interpretation of the data, however, is complicated by the profound effect of the electric charges upon the rate. The modern theory of electrolytes predicts that the presence of electric charges will affect the number of rate determining collisions in two ways: (a) through the electrical repulsion (or attraction) between reactants and (b) through the ionic atmosphere (Brönsted primary salt effect) which disturbs the statistical distribution of the reactant ions as a function of the concentration of all ions in the system.

The objective of this paper is to employ procedures which correct the thermodynamic factors determining the rate of reaction, namely, the energy and entropy of activation for electrostatic contributions so that the rate calculated for uncharged molecules of the same chemical characteristics as the reactant ions may be compared with the predictions of the collision theory.

The frequency factor, B, in the integrated form of the Arrhenius equation

$$\log k = B - \frac{\Delta E^*}{2.3RT} \qquad (1)$$

determines the rate at which molecules endowed with the energy of activation ΔE^* react. B is related to ΔE^* through the relation[1]

$$2.3RB = \int_0^T \frac{\partial \Delta E^*}{\partial T} \frac{dT}{T} + 2.3R \log \nu \qquad (2)$$

where ν is a frequency.

(1) La Mer. J. Chem. Phys., 1, 289 (1933).

Setting[2] $\nu = kT/h$ then the integral term in eq. (2), designated hereafter as ΔS^*, becomes the entropy of activation for all degrees of freedom. For ionic reactions it will be expedient to decompose ΔS^* into a non-electrical and an electrical part

$$\Delta S^* = \Delta S_0^* + (\Delta S_D^* + \Delta S_{In.}^*) \qquad (3)$$

Thus ΔS_0^* refers to the entropy contribution for the reactants as uncharged molecules. ΔS_D^* arises from the presence of electric charges upon the reactant ions alone, whereas $\Delta S_{In.}^*$ is the interaction contribution of the ionic atmosphere.

By combining eq. (1) with the Brönsted–Debye–Hückel limiting equation

$$\log k = \frac{2z_A z_B \beta \sqrt{\mu}}{(DT)^{3/2}} + \log k_{\sqrt{\mu} = 0} \qquad (4)$$

La Mer and Kamner[3] derived the following expressions for the contributions of the ionic atmosphere to B and ΔE^* valid for small values of the ionic strength, μ

$$\frac{\Delta E_{In.}^*}{2.3RT} = -\frac{2z_A z_B \beta \sqrt{\mu}}{(DT)^{3/2}} \left[\frac{3}{2} \frac{\partial \ln D}{\partial \ln T} + \frac{1}{2} \frac{\partial \ln V}{\partial \ln T} + 3/2 \right] \qquad (5)$$

$$\frac{\Delta S_{In.}^*}{2.3R} = -\frac{2z_A z_B \beta \sqrt{\mu}}{(DT)^{3/2}} \left[3/2 \frac{\partial \ln D}{\partial \ln T} + 1/2 \frac{\partial \ln V}{\partial \ln T} + 1/2 \right] \qquad (6)$$

In these equations β equals 1.816×10^6 and is a constant independent of the temperature, z is the

(2) Eyring. ibid., 3, 107 (1935); Chem. Rev., 17, 65 (1935).

(3) La Mer and Kamner. THIS JOURNAL, 57, 2662 (1935). See also Moelwyn-Hughes. Proc. Roy. Soc. (London), 155, 308 (1936); A157, 667 (1936), for substantially identical equations, derived more explicitly by means of the collision theory.

net charge on the ion, D is the dielectric constant, V is the volume and R and T have their usual significance.

By introducing Wyman's[4] values for D and $\partial \ln D/\partial \ln T$ and the "I.C.T."[5] values for $\partial \ln V/\partial \ln T$, eqs. (4), (5) and (6) assume the form

$$\log k = z_A z_B A_1 \sqrt{\mu} + \log k_{\sqrt{\mu}\,=\,0} \qquad (7)$$

$$\frac{\Delta E^*_{\text{In.}}}{2.3RT} = z_A z_B A_2 \sqrt{\mu} \qquad (8)$$

$$\frac{\Delta S^*_{\text{In.}}}{2.3R} = z_A z_B A_3 \sqrt{\mu} \qquad (9)$$

where A_1 is 0.977, 1.014 and 1.060 at 5, 25 and 45°; A_2 is 0.45, 0.52 and 0.60 at 15, 25 and 35°; A_3 is 1.44, 1.53 and 1.64 at 15, 25 and 35°, respectively for water. La Mer and Kamner[3] reported data on the bromoacetate–thiosulfate reaction which supported these limiting laws.

For a given temperature the rate of ionic reactions *in high dielectric solvents* can be expressed by the Christiansen[6]–Scatchard[7] equation

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

k_∞ is the value of the molar rate constant extrapolated to a medium of infinite dielectric constant where all electrostatic effects vanish. Extrapolating $\log k$ as a function of κ[8] to $\kappa = 0$ eliminates the last term representing the primary salt effect. By plotting these values of $\log k_{\kappa\,=\,0}$ against $1/D$ and extrapolating to infinite dielectric constant ($1/D = 0$) yields k_∞.

From the slope one can determine readily the parameter ($r_A + r_B$) representing the distance of approach of the centers of the reactant ions when the chemical process occurs. Since $-\Delta F^*/2.3\,RT = \log k - \log v$, multiplication of each term in eq. (10) by ($-2.3\,RT$) and adding the frequency term $2.3RT \log (kT/h)$ to both sides yields the respective contributions to the free energy of activation designated by the subscripts 0, D and In. Thus each term of eq. (10) can be identified respectively as

$$\frac{\Delta F^*}{2.3RT} = \frac{\Delta F^*_0}{2.3RT} + \frac{\Delta F^*_D}{2.3RT} + \frac{\Delta F^*_{\text{In.}}}{2.3RT} \qquad (11)$$

By applying the Arrhenius equation to decom-

(4) Wyman. *Phys. Rev.*, **35**. 623 (1930).

(5) "International Critical Tables." first edition, Vol. III. McGraw-Hill Book Co., Inc., New York, 1926, p. 25.

(6) Christiansen. *Z. physik. Chem.*, **113**, 35 (1924).

(7) Scatchard. THIS JOURNAL, **52**, 52 (1930); *Chem. Rev.*, **10**, 229 (1932).

(8) The Debye κ is related to the ionic strength by the equation

$$\kappa = \sqrt{\frac{8\pi\epsilon^2 N}{DRT}}\,\sqrt{\mu}$$

pose the free energy of activation into the corresponding entropy and energy equivalents, it follows that[9]

$$\Delta E^*_D = \Delta F^*_D \left[1 + \frac{T}{D}\frac{\partial D}{\partial T} \right] \qquad (12)$$

$$\Delta S^*_D = \frac{\Delta F^*_D}{T} \left[\frac{T}{D}\frac{\partial D}{\partial T} \right] \qquad (13)$$

When the entropy of activation is determined by measuring the temperature coefficient at constant dielectric constant by the use of isodielectric solvents, the contribution ΔS^*_D vanishes since $\partial D/\partial T = 0$. The contribution $\Delta S^*_{\text{In.}}$ can be eliminated by employing in the Arrhenius equation the values of $\log k$ extrapolated to $\kappa = 0$. One thus obtains a value of B for an ionic reaction which has been freed from all electrostatic contribution to the entropy of activation arising from the net charges of the ions; *i. e.*, the value of B thus calculated should represent the frequency factor for a reaction between uncharged molecules possessing the same chemical characteristics as the ions. This procedure readily permits the comparison of data obtained for an ionic reaction with that predicted by the collision theory for a reaction between uncharged molecules.

On the contrary ΔE^*_D does not vanish when $\partial D/\partial T = 0$, but is equal to the corresponding free energy contribution, *i. e.*

$$\Delta E^*_D = \Delta F^*_D = -\frac{z_A z_B N \epsilon^2}{D}\left(\frac{1}{r_A + r_B} \right) = \text{Constant.}\,\frac{1}{D} \qquad (14)$$

Thus eq. (14) specifies either the *electrical work* or the *potential energy* per mole involved in bringing a reactant ion A up to a reactant ion B in the absence of an ionic atmosphere. The entropy contribution which arises in the electrical interaction between such an *isolated* pair of ions originates solely from the temperature dependence of the dielectric, and it is this entropy contribution which vanishes when the temperature coefficient is determined in isodielectric solvents.

Svirbely and Warner[10] first called attention to the importance of determining critical increments in isodielectric media but do not treat the entropy contributions. In their notation the quantity $(E^{0*})_D \equiv 2.3\,RT\,(\partial \log k_0/\partial T)_D$ and designated by them as the true energy of activation is the same as our

(9) La Mer. *J. Franklin Inst.*, **225**, 709 (1938). This paper contains two misprints. In eq. (32), ΔS^*_D should read $\Delta F^*_D/T$ as in eq. (13) below. Eq. (25) should read $\log k =$ etc., instead of $B =$ etc.

(10) Svirbely and Warner, THIS JOURNAL, **57**, 1883 (1935).

$$\Delta E_0^* + \Delta E_D^* - \frac{N\epsilon^2 z_A z_B}{D}\left(\frac{1}{r_A + r_B}\right)\frac{T}{D}\frac{\partial D}{\partial T} \equiv \Delta E_0^* + \frac{N\epsilon^2 z_A z_B}{D}\left(\frac{1}{r_A + r_B}\right) \quad (15)$$

If the ions are not rigid monopoles as implied in the theoretical model but actually possess superimposed dipoles, there will be additional terms in eq. (10). Since the dipole contributions to the Brönsted primary salt effect will vanish as a function of higher order in the concentration than will the monopole contributions, this effect will be eliminated by extrapolating to $\kappa = 0$.

The attraction (or repulsion) between the reactant ions exerted by the dipoles will still persist after extrapolation to $\kappa = 0$. This effect should vary inversely with D and hence will be reflected in an abnormal value of the parameter $(r_A + r_B)$ determining the slope of log $k_{\kappa = 0}$ vs. $1/D$. When the ions are also dipolar, the Debye–Hückel interaction parameter, a, will not equal $(r_A + r_B)$ as was assumed in the derivation of eq. (10).

Since the fading of brom phenol blue in alkali is an ionic reaction which can be followed accurately and conveniently by colorimetric methods, it is well suited to test the theories set forth above.

The Fading of the Phthalein Dyes

The kinetics of the fading in alkali of various phthaleins and sulfonphthaleins have been studied by many investigators,[11-15] and particularly by Thiel. All of these authors regard the process as the addition of hydroxyl ion to the dye ion to form a colorless carbinol. Lund[14] first suggested comparison with the Brönsted–Debye limiting law as a means of determining the electric charge type of this reaction. Recently Panepinto and Kilpatrick[16] found for the brom phenol blue fading reaction that the slope of the log k vs. $\sqrt{\mu}$ curve conforms closely to that required for a reaction between a divalent negative tetrabromosulfonphthalein ion and a hydroxyl ion. Hence it is of the same electric charge type as the bromoacetate–thiosulfate reaction used previously by La Mer and Kamner to test eqs. (4) to (9).

(11) Kober and Marshall, THIS JOURNAL, 33, 59 (1911).

(12) Biddle and Porter, ibid., 37, 1571 (1915).

(13) A. Thiel, Monatsh., 53/54, 1008 (1929).

(14) Lund, J. Chem. Soc., 1844 (1930).

(15) Kolthoff, "Acid Base Indicators," The Macmillan Company, New York, 1937, translated by Rosenblum from the fourth (1931) German edition. See pages 111, 116, and 218–227 for a résumé of the theory of the fading of phthalein and sulfonphthalein dyes up to 1931.

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

Panepinto and Kilpatrick, however, without considering the literature, advance an entirely different mechanism[17] for the kinetic process, namely, the substitution of one of the four bromine atoms by hydroxyl ion yielding bromide ion. They give twenty-one determinations for bromide ion in the faded brom phenol blue solution which are in fair agreement with the predictions of their substitution mechanism, but give no details of their analytical methods.

Although we have repeatedly varied conditions over wide ranges, we have never been able to obtain precipitation of silver bromide upon the addition of silver nitrate to a faded dye solution acidified with dilute nitric acid as would be expected if bromide ion were present. The addition of potassium bromide $(10^{-5}m)$ to the faded dye solution, however, yielded promptly with silver nitrate a precipitate of silver bromide.

Positive evidence that the addition mechanism and not the substitution mechanism is correct is supplied by the following observations. We find, in agreement with previous workers, that the fading of phenolphthalein is a reversible process. The position of equilibrium depends upon the concentration of alkali. In the case of brom phenol blue, the fading process goes sensibly to completion at the sodium hydroxide concentrations employed. That the reverse process exists but is exceedingly slow in alkaline solutions can be demonstrated as follows. When an alkaline faded brom phenol blue solution is acidified to pH 2, the characteristic yellow acid color of brom phenol blue develops progressively with time. When aliquots of the light yellow colored solution are made slightly alkaline, the characteristic blue color of brom phenol blue is regenerated promptly; the depth of the blue color varies with the time elapsed following acidification. These observations are consistent with the view that the addition of the hydroxyl ion in strongly alkaline solution to form a carbinol and the subsequent removal of hydroxyl in acid solution to regenerate the acid form of the dye are slow reversible processes.

Through the courtesy of the Editor, the pertinent pages of Panepinto's typewritten dissertation have been made available to us since this paper was written. It now appears that Panepinto and Kilpatrick likewise did not obtain an

(17) This mechanism had been proposed previously by Chase and Kilpatrick, ibid., 54, 2284 (1932); and by Kilpatrick, Chem. Rev., 16, 57 (1935).

immediate precipitate of silver bromide. After a minimum of three days' standing, the precipitate which forms slowly was filtered off and the silver bromide content determined.

It should be obvious that Panepinto and Kilpatrick's procedure yields silver bromide as a result of the slow removal of the bromine attached to carbon by the action of silver ion, a reaction which is well known from the investigations of Burke and Donnan and of Euler[18] as well as from the work of more recent authors on the action of mercuric nitrate upon organic halides.[19] Panepinto and Kilpatrick's analytical data are beside the point and do not furnish competent evidence for the substitution mechanism.

Experimental

The brom phenol blue (B. P. B.) used in this investigation was Eastman (E. K. C.) No. 752 tetrabromophenolsulfonphthalein. Analyses made by Mr. Gottlieb of these Laboratories gave

	Found		Average	Theoretical
% bromine	47.92	47.59	47.75	47.73
% sulfur	4.94	4.81	4.88	4.77

A stock solution 2×10^{-4} molar in B. P. B. was prepared by dissolving the dye in alcohol, adding sodium hydroxide for conversion to the monosodium salt, evaporating to dryness, and diluting with water. Kinetic checks using a Hynson, Westcott and Dunning (H. W. D.) and also a LaMotte preparation yielded the following k_N values for 0.009 N sodium hydroxide at 25°: E. K. C., 0.3336; H. W. D., 0.3326; LaMotte, 0.3331. The analyses and the kinetic concordance between different preparations furnish convincing proof of the purity of the dye employed.

The sodium hydroxide solution was freed from carbonate by the addition of a trace of barium hydroxide, standardized against B. S. potassium acid phthalate and stored in a paraffin lined bottle protected from carbon dioxide.

Absolute ethyl alcohol was refluxed with lime and potassium hydroxide for four hours, followed by distillation after the addition of metallic sodium. C. P. methyl alcohol was treated similarly, and the fractions boiling at 78.4 and 64.8° at 761.9 mm. were retained.

All volumetric apparatus was calibrated. The thermostats were constant to ±0.005°, and were standardized against a B. S. platinum resistance thermometer. In all except the most rapid runs the bottles containing the fading mixtures were blackened to prevent possible catalysis by light. Comparison runs in unblackened flasks exhibited no abnormalities.

The experiments were performed by diluting the alkali solutions with solvent, adding the dye solution and adjusting the final volume to make the dye 2×10^{-5} molar. The colorimetric standards were made up fresh from stock solutions of alkali and of dye for each set of observations.

(18) Euler. Ber., 39, 2726 (1906).
(19) Roberts and Hammett, THIS JOURNAL, 59, 1063 (1937).

One observer read the scale and recorded the results of five settings made by a second observer using a Bausch and Lomb Hastings type colorimeter. The observers then exchanged places and made five additional settings as promptly as possible. A Palo-Myers daylight lamp with a blue filter furnished the illumination. The time consumed in transferring a sample from the reaction flask to the colorimeter and making these ten readings was about two minutes. Any perceptible fading of the unknown during the short periods of observation should be exactly compensated by the same fractional fading of the standard. The high precision and reproducibility of the rate constants undoubtedly are due to this fortunate circumstance of a first order rate constant. The dielectric constants of the water–alcohol mixtures were taken from Åkerlöf.[20]

Data

Typical examples are given in Tables I and II. They demonstrate that the individual k_N values calculated for a first order reaction are constant to 60% conversion. In those alcoholic media where the rate of fading is very slow, k_N exhibits a

TABLE I

KINETICS OF THE FADING OF BROM PHENOL BLUE IN WATER

Temp. 25°. NaOH, 0017 N.   Temp. 5°. NaOH, 0.013 N.

Days	$10^5 \times$ concn. of B. P. B.	k_N	Days	$10^5 \times$ concn. of B. P. B.	k_N
0.5375	1.24	0.7422	1.528	1.67	0.1159
.6912	1.19	.7464	1.912	1.59	.1179
.8806	1.04	.7427	2.532	1.49	.1153
.9113	1.01	.7465	2.672	1.47	.1151
.9507	0.98	.7448	3.643	1.32	.1139
.9931	0.95	.7428	5.542	1.04	.1169
1.062	0.91	.7427	7.983	0.80	.1136
		Av. 0.7440			Av. 0.1155

$$k = \frac{0.7440}{0.017} = 43.76 \qquad k = \frac{0.1155}{0.013} = 8.885$$

TABLE II

KINETICS OF THE FADING OF BROM PHENOL BLUE IN WATER–ALCOHOL

EtOH, 23.5 wt. %. D; 64.86; temp., 25°; NaOH, 0.09 N.   MeOH, 29.52 wt. %; D, 64.55; temp., 25°; NaOH, 0.09 N.

Days	$10^5 \times$ concn. of B. P. B.	k_N	Days	$10^5 \times$ concn. of B. P. B.	k_N
0.09028	1.87	0.6842	0.5243	1.33	0.7661
.7067	1.23	.6854	.5670	1.30	.7643
.7203	1.21	.6867	.7436	1.13	.7588
.8040	1.15	.6874	.7802	1.10	.7663
.8540	1.11	.6861	.8962	1.00	.7659
.9150	1.07	.6836	.9345	0.98	.7614
1.0450	0.99	(.6734)	1.031	0.91	.7584
		Av. 0.6856	1.548	0.62	(.7480)
					Av. 0.7630

$$k = \frac{0.6856}{0.09} = 7.618 \qquad k = \frac{0.7630}{0.09} = 8.478$$

(20) Åkerlöf. ibid., 54, 4125 (1932).

very small decrease with time after 60% conversion, at which point the reverse reaction becomes perceptible. Dividing k_N by N, the normality of the sodium hydroxide which is sensibly constant throughout a given run, yields k, the bimolecular constant for that run. The time unit is in days.
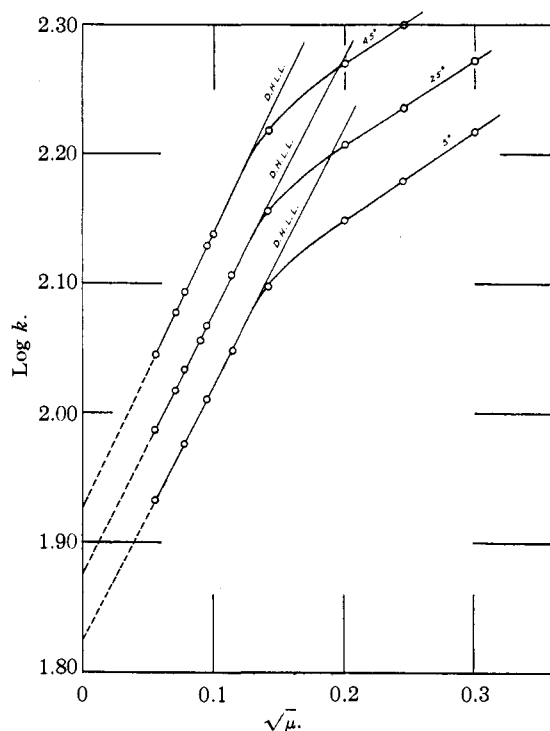

Fig. 1.—Velocity constant of the reaction (B. P. B.)⁻ + OH⁻ as a function of ionic strength. Log $k_{25}°$ = log $k_{45}°$ − 0.50. Log $k_5°$ = log $k_{45}°$ −1.10.

The velocity constants, the energy of activation and the entropy of activation as a function of ionic strength and of temperature are tabulated in Table III. The plots of log k, ΔE^* and B, respectively, against the square root of the ionic strength are given in Figs. 1, 2, and 3. Log k obeys the limiting law to a higher ionic strength ($\sqrt{\mu}$ = 0.12) than is justified on the basis of the function $[\kappa/(1 + \kappa a)]$ in eq. (10). This is shown in the more sensitive plot, Fig. 4, where values of log $k_{\kappa = 0}$ calculated for the values of the parameter a = 2, 4 and 5 Å. are plotted against $\sqrt{\mu}$. The maximum at $\sqrt{\mu}$ = 0.14 in Fig. 4 is reminiscent of the type of curve obtained for the activity coefficient function for mixtures of higher valence type,[21,22] when the contribution of terms higher than the Debye approximation are neglected as is the case in eq. (10). The calculation

(21) La Mer and Mason. THIS JOURNAL. 49, 410, 363 (1927).
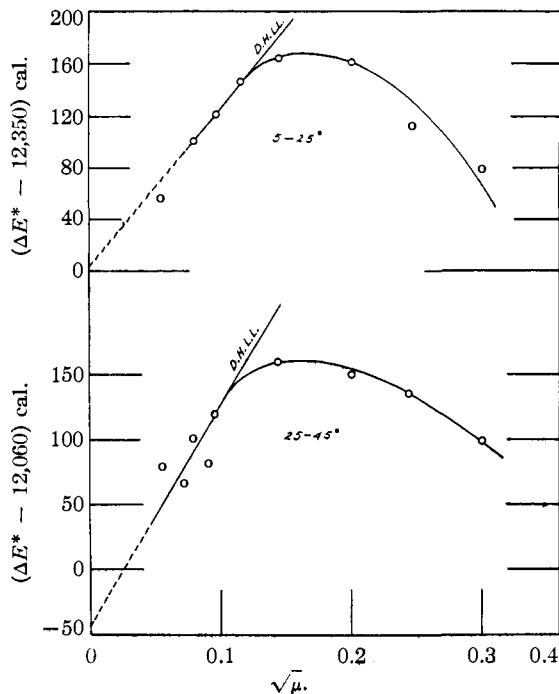(22) La Mer, Gronwall and Greiff, J. Phys. Chem., 35, 2245 (1931).

Fig. 2.—Energy of activation of the reaction (B. P. B.)⁻ + OH⁻ as a function of ionic strength.

of these corrections with a single a value in the complicated case of reaction velocity is not only tedious but not entirely warranted under the assumption $r = a$ for ions have differing radii. A graphical extrapolation is sufficient for our purposes.
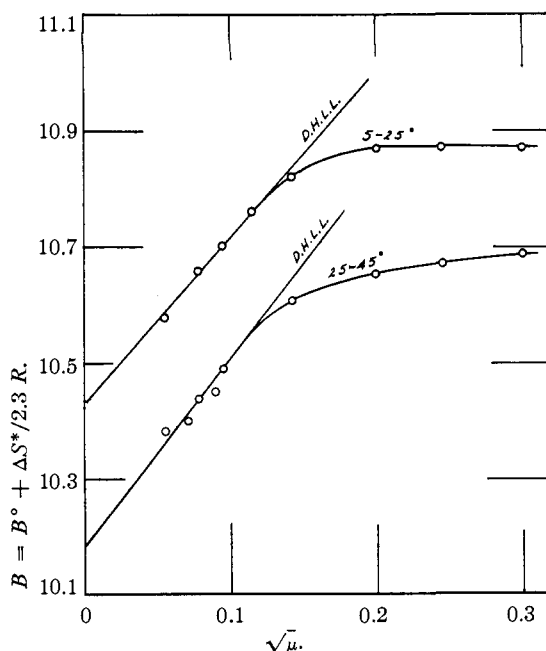

Fig. 3.—Entropy of activation for the reaction (B. P. B.)⁻ + OH⁻ as a function of ionic strength.

TABLE III

DATA FOR WATER[a]

Normality of NaOH	$\sqrt{\mu}$	$k_{5°}$	$k_{25°}$	$k_{45°}$	ΔE^* 5–25°	ΔE^* 25–45°	B 5–25°	B 25–45°
0.000	(0.0000)	(5.25)	(23.6)	(85.1)	(12,350)	(12,100)	(10.46)	(10.16)
.003	.0551	6.81₀	30.67	111.₁	12,407	12,13₈	10.58	10.38
.005	.0710		33.0₆	119.₆		12,127		10.40
.006	.0777	7.55₃	34.2₁	124.₂	12,45₁	12,16₁	10.66	10.44
.008	.0897		36.1₅	131.₀		12,142		10.45
.009	.0951	8.14₉	36.9₉	134.₆	12,47₂	12,17₉	10.70	10.49
.013	.1142	8.88₅	40.4₆		12,49₈		10.76	
.017	.1305		43.7₆					
.02	.1415	9.92₅	45.2₉	165.₂	12,51₅	12,22₀	10.82	10.61
.04	.2001	11.1₈	50.9₈	186.₁	12,51₂	12,20₉	10.87	10.65
.06	.2450	12.0₀	54.3₂	198.₀	12,464	12,19₆	10.87	10.67
.09	.3000	13.1₁	59.2₁	215.₀	12,43₀	12,15₉	10.87	10.69

[a] Calculations upon the precision of ΔE^* show that in the range 5–25° the probable error in ΔE^* varies from 11 to 55 cal. with an average value of 27 cal. In the range 25–45° the probable error varies from 9 to 104 cal. and averages 50 cal.

The agreement up to $\sqrt{\mu} = 0.12$ with the limiting laws derived by La Mer and Kamner[3] for ΔE^* and B is all that can be expected and demonstrates that the fading reaction obeys the electrostatic theory not only in respect to the free energy of activation, but also in respect to energy of activation and entropy of activation.
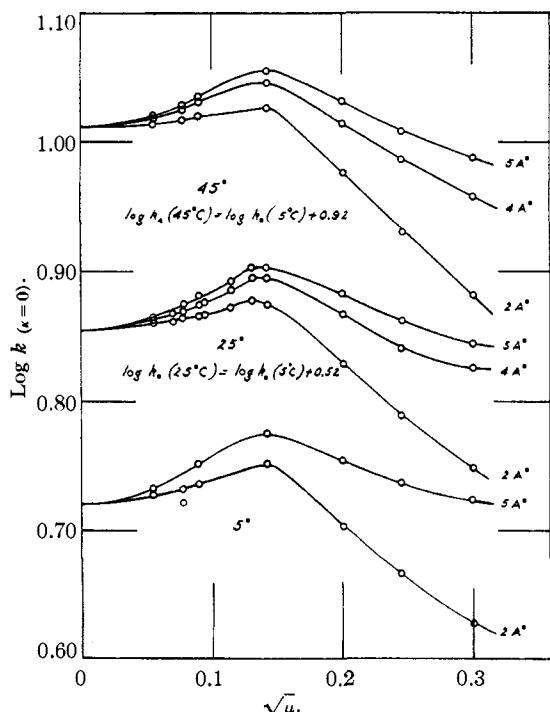

Fig. 4.—Log $k_{\kappa = 0}$ of the reaction (B. P. B.)⁻ + OH⁻ as a function of ionic strength.

This conclusion conflicts with Panepinto and Kilpatrick's[16] finding that the values of ΔE^* do not exhibit the increase with concentration pre-

dicted by the limiting law,[23] eq. (8). Panepinto and Kilpatrick's values for log k at 25° parallel ours when plotted against $\sqrt{\mu}$ but are uniformly 0.080 unit larger (20% in k). Their values of ΔE^* calculated for five degree intervals, however, range between 11,600 and 13,600 cal. (ref. 16, Table V, p. 1873) with an average value of 12,500 ± 500 cal. The fact that ΔE^* passes through a maximum value at $\sqrt{\mu} = 0.16$ which is only 160 cal. greater than ΔE_0^* shows that their data are not sufficiently reproducible to warrant any comparison with the theoretical predictions for the concentration dependence of ΔE^*. Panepinto and Kilpatrick's discussion is tantamount to stating that their data obey the limiting law in its free energy form but disobey it in terms of the

TABLE IV

DATA FOR ETHYL ALCOHOL–WATER AND FOR METHYL ALCOHOL–WATER AT 25°

Normality of NaOH, 0.009; $\sqrt{\mu} = 0.0950$; and $a = 5$ Å.

Wt. % of EtOH	D	$1/D$	k	$k_{\kappa = 0}$	Log $k_{\kappa = 0}$
0.00	78.5	0.0127	37.0	25.2	1.401
10.2	72.5	.0138	14.9	9.71	0.987
15.4	69.5	.0144	8.60	5.46	.737
20.6	66.5	.0150	4.89	3.01	.479
31.5	60.0	.0167	1.70	0.103	$\bar{1}$.013

Wt. % of MeOH	D	$1/D$	k	$k_{\kappa = 0}$	Log $k_{\kappa = 0}$
0.00	78.5	0.0127	37.0	25.2	1.401
8.07	74.8	.0134	24.2	16.1	1.207
16.2	71.0	.0141	13.9	8.93	0.951
24.7	67.0	.0149	6.99	4.33	.637
38.0	60.6	.0165	2.94	1.69	.228
42.8	52.8	.0189	1.83	0.107	$\bar{1}$.029

(23) Panepinto and Kilpatrick refer only to Moelwyn-Hughes's equation for the limiting law dependence upon concentration. Comparison however shows that their eq. (13) is identical with that given earlier by La Mer and Kamner.[1]

TABLE V
WATER AND ETHYL ALCOHOL–WATER MEDIA

Constant composition, variable dielectric (√μ̄ = 0.1415) — columns for H₂O, EtOH 12.33 Wt.%, EtOH 24.03 Wt.%. Isodielectric, variable composition — columns for √μ̄ = 0.300 (D = 71.42), D = 64.86, √μ̄ = 0.1415 (D = 71.42).

Temp. °C	H₂O			EtOH 12.33 Wt.%		EtOH 24.03 Wt.%		√μ̄ = 0.300, D = 71.42		D = 64.86		√μ̄ = 0.1415, D = 71.42	
	k	D	k	D	k	D	k	Wt.% of EtOH	k	Wt.% of EtOH	k	Wt.% of EtOH	k
5	9.925	86.28	13.11	78.74	6.018	71.42	1.785	24.03	1.782	34.25	0.5567	24.03	1.388
25	45.29	78.54	59.21	71.42	23.37	64.55	7.314	12.33	23.37	23.51	7.618	12.33	17.99
45	165.2	71.42	215.0	64.86	76.11	58.49	26.03	0.00	215.0	12.33	76.11	0.00	165.2
B_{5-25}	10.82		10.88		9.56		9.38		(16.91)		16.68		16.72
B_{25-45}	10.60		10.68		9.53		9.64		16.70		16.78		16.68
ΔE^{*}_{5-25}	12,520		12,430		11,190		11,630		21,220		21,570		21,120
ΔE^{*}_{25-45}	12,200		12,140		11,130		11,970		20,930		21,700		21,060

TABLE VI
METHYL ALCOHOL–WATER MEDIA

Constant composition, variable dielectric — columns for MeOH 15.15 Wt.%, MeOH 29.52 Wt.%. Isodielectric, variable composition (√μ̄ = 0.300) — D = 71.42, D = 64.86, and √μ̄ = 0.1415 (D = 71.42).

Temp. °C	MeOH 15.15 Wt.%		MeOH 29.52 Wt.%		√μ̄ = 0.300, D = 71.42		D = 64.86		√μ̄ = 0.1415, D = 71.42	
	D	k	D	k	Wt.% of MeOH	k	Wt.% of MeOH	k	Wt.% of MeOH	k
5	78.77	5.694	71.42	1.892	29.52	1.892	42.67	0.672	29.52	1.483
25	71.42	24.11	64.55	8.478	15.11	24.11	29.20	8.758	15.15	18.46
45	64.86	87.38	58.49	37.97	0.00	215.0	15.15	83.38	0.00	165.2
B_{5-25}		10.10		9.97		(16.75)		16.45		16.49
B_{25-45}		10.28		11.29		16.50		16.48		16.51
ΔE^{*}_{5-25}		11,900		12,360		20,980		21,170		20,790
ΔE^{*}_{25-45}		12,140		14,140		20,630		21,220		20,180

internal energy. That such a statement will encounter theoretical obstacles is manifest when it is recognized that the expression for ΔE^{*} is obtained from ΔF^{*} by introducing the temperature derivative of the same analytic expression for D as a function of T as was employed in ΔF^{*} and found to be in agreement with experiment.

The maximum in the ΔE^{*} curves above the range of validity of the limiting law is reminiscent of many curves for the heat of dilution,[24] notably for potassium nitrate and iodate. Parallel behavior should obtain since the concentration dependence of ΔE^{*} corresponds to the heat of dilution of the activation process. No generally accepted theory for the peculiarities of the heats of dilution at high concentrations exists.

The data in water–alcohol solutions have been extrapolated to $\kappa = 0$ assuming $a = 5$ Å. in the last term of eq. (10). The values of log $k_{\kappa = 0}$ are plotted against $1/D$ in Fig. 5. For $D > 65$ the linear relationship holds, yielding slopes corresponding to 2.81 and 3.43 Å. for the parameter $(r_A + r_B)$ in the presence of ethyl and methyl alcohols, respectively. For $D < 65$ the curves exhibit a rapid change of slope comparable to that observed by Tomlinson and La Mer,[25] for the

(24) Lange and Robinson, Chem. Rev., 9, 89 (1931). See Fowler, "Statistical Mechanics," 2d ed., The Macmillan Co., 1936, pp. 546–548.

(25) Tomlinson and La Mer, in press.

bromoacetate–thiosulfate reaction for $D < 70$.

The data for k, ΔE^{*} and B as determined in media of constant composition and isodielectric media are assembled in Tables V and VI. Both ΔE^{*} and B vary according to eqs. (12) and (13) when determined at constant composition. When
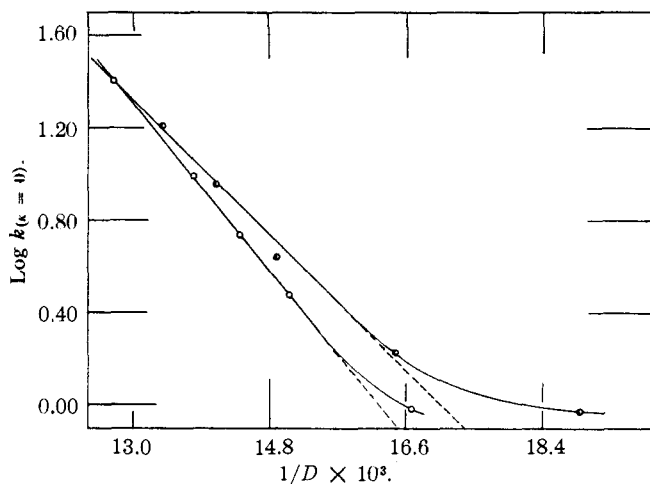

Fig. 5.—Log $k_{\kappa = 0}$ at 25° for the reaction (B. P. B.)⁻ + OH⁻ versus the reciprocal of the dielectric constant of the media: O, C₂H₅OH–H₂O; ●, CH₃OH–H₂O.

D is held constant, ΔE^{*} varies as predicted by eq. (12). However, if we exclude the two values in parentheses which involve relatively slow rates and hence may be somewhat in error, B is also constant in agreement with eq. (13). $\Delta S^{*}_{In.}$ does not vary much with concentration changes

in the range $\sqrt{\mu} = 0.142$ to 0.300 (Fig. 3).

The data of Svirbely and Schramm[26] on the reaction between ammonium and cyanate ions are also in agreement with eqs. (12) and (13). These authors noted that B (log K in their notation) was remarkably constant when $\partial D/\partial T = 0$ but give no explanation for this constancy. The agreement between their results and ours is significant since their reaction involves reactant ions of opposite sign.[27]
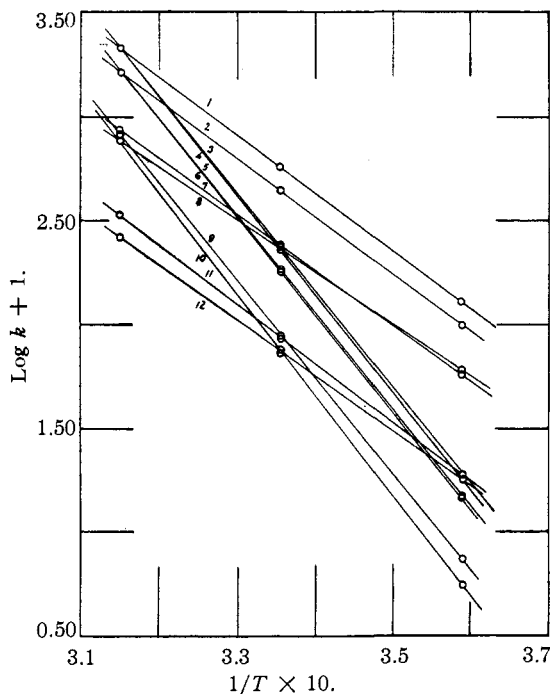

Fig. 6.—Log k as a function of $\sqrt{\mu}$ in media of constant composition and in isodielectric media.

In constant composition media, variable dielectric.

No.	$\sqrt{\mu}$	% Alcohol	ΔE^* 5-25°	25-45°	B 5-25°	25-45°
1	0.3000	0	12.430	12.140	10.88	10.68
2	.1415	0	12.520	12.200	10.82	10.60
7	.3000	15.15 MeOH	11.900	12.140	10.10	10.28
11	.3000	29.52 MeOH	12.360	14,140	9.97	11.29
8	.3000	12.33 EtOH	11.190	11.130	9.56	9.53
12	.3000	24.03 EtOH	11.630	11.970	9.38	9.64

In isodielectric media where $\partial D/\partial T = 0$.

No.	$\sqrt{\mu}$	D H₂O-MeOH media	ΔE^* 5-25°	25-45°	B 5-25°	25-45°
5	0.1415	71.42	20,790	20,810	16.49	16.51
3	.3000	71.42	20,980	20,630	(16.75)	16.50
9	.3000	64.86	21,170	21,220	16.45	16.48
		H₂O-EtOH media				
6	0.1415	71.42	21,120	21,060	16.72	16.68
4	.3000	71.42	21,220	20,930	(16.91)	16.70
10	.3000	64.86	21,570	21,700	16.68	16.78

(26) Svirbely and Schramm, THIS JOURNAL. **60**, 330 (1938).

(27) In a more recent paper, Lander and Svirbely [ibid.. **60**, 1613 (1938)] find that in isodielectric glycol-water media the B values gradually increased with increasing dielectric constant.

In Fig. 6 log k is plotted against $1/T$ from data in Tables V and VI. A small solvent effect is noticeable.

In the notation of the collision theory, the molal rate constant is given by the expression

$$k = PZ^0 e^{-\Delta E^*/RT} \qquad (16)$$

where

$$Z^0 = \frac{N}{1000} \sigma_{12}^2 \left[8\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2} \right) \right]^{1/2} \qquad (17)$$

is the gas kinetic collision frequency, σ_{12} is the distance of approach between centers of reactants for an effective collision, N is Avogadro's number, M_1 and M_2 are the molecular weights of the reactants, and P represents the deviation from theory.

The thermodynamic rate theory using $\nu = RT/Nh$ is

$$k = \frac{RT}{Nh} e^{\Delta S^*/R} e^{-\Delta E^*/RT} \qquad (18)$$

whence

$$PZ^0 = \frac{RT}{Nh} e^{\Delta S^*/R} \qquad (19)$$

A test of the collision theory in terms of the thermodynamic theory can be made either by assuming a value for σ_{12} and calculating P or by assuming $P = 1$ and calculating the value of σ_{12} which must be employed to give agreement with the gas kinetic theory.

Inserting numerical values for the constants in eqs. (17) and (19), under the assumption that $P = 1$, yields

$$\log \sigma_{12} = \frac{1}{2} \left(\frac{\Delta S^*}{2.3R} \right) + \frac{1}{2} \log \left[\frac{M_1 M_2}{M_1 + M_2} \right]^{1/2} - 6.9425 \qquad (20)$$

Introducing the molecular weight of the unhydrated ions ($M_1 = 17$, and $M_2 = 668$) eq. (20) for the present reaction becomes

$$\log \sigma_{12} = \frac{1}{2} \left(\frac{\Delta S^*}{2.3R} \right) - 6.6376 \qquad (21)$$

Since from eq. (2)

$$\frac{\Delta S^*}{2.3R} = B - \log \frac{RT}{hN} \qquad (22)$$

eq. (21) becomes

$$\log \sigma_{12} = \frac{1}{2} \left(B - \log \frac{RT}{hN} \right) - 6.6376 \qquad (23)$$

Substituting $B = 16.71$ (days^{-1}) and 16.49 (days^{-1}) for ethyl and methyl alcohol additions,

respectively, from Tables V and VI and log RT/hN = 17.731 (days^{-1}), gives σ_{12}, equal to 7.10 and 5.51 Å., respectively, as the gas–kinetic collision diameters in the two solvents. If on the other hand it is assumed that the values of $(r_A + r_B)$ = 2.81 and 3.43 Å. (see Fig. 5), respectively, are the proper values for σ_{12}, then P = 6.38 and 2.58, respectively.

It is evident that the fading reaction obeys not only the requirements of the electrostatic theory but also those of the simple collision theory within a small factor that can be attributed to specific solvent effects, and the selection of a proper molecular weight for hydrated ions.

The energy of activation freed from all net charge contributions, i. e., ΔE_0^*, can be calculated from the Arrhenius equation by employing isodielectric solvents as follows. In analogy to eqs. (3) and (11) the energy of activation, ΔE^*, can be written as

$$\Delta E^* = \Delta E_0^* + \Delta E_D^* + \Delta E_{In}^*. \qquad (24)$$

When κ = 0, ΔE_{In}^* vanishes and when determined in isodielectric solvents

$$\Delta E_D^* = \Delta F_D^* = -2.3RT \log k_D \qquad (25)$$

from eq. (12). Therefore

$$\Delta E_0^* = \Delta E^* + 2.3RT \log k_D \qquad (26)$$

The average of the slopes in methyl and ethyl alcohol of log $k_{\kappa = 0}$ vs. $1/D$ in Fig. 5 is -357. Hence log k_D (at $1/D$ = 0.013) = -4.64. ΔE^* in isodielectric solvents is 21,100 from Tables V and VI. Hence at 25°

$$\Delta E_0^* = 21{,}100 + 1365\ (-4.64) - \Delta E_{In}^* =$$
$$15{,}170\ \text{cal.} - 120\ \text{cal.} = 15{,}050\ \text{cal.}$$

Conclusions

1. The kinetics of fading of brom phenol blue (tetrabromophenolsulfonphthalein) in alkali have been investigated in water and in methyl and ethyl alcohol solutions containing 0.003 to 0.09 N sodium hydroxide at 5, 25 and 45° to determine the energy and entropy of activation for media of constant composition and also for constant dielectric constant.

2. The reaction involves the addition of hydroxyl ion to the divalent negative dye ion. No evidence could be obtained in support of the view that the kinetic process involves the substitution of bromine by hydroxyl ion, forming bromide ion.

3. When the ionic strength is less than 0.014, the reaction obeys the limiting laws for the electrostatic contributions to the free energy, energy and entropy of activation derived by La Mer and Kamner from the Brönsted theory of reaction velocity and the Debye–Hückel theory of electrostatic interaction.

4. The energy of activation is dependent upon temperature (T), ionic strength (μ) and dielectric constant (D) when determined either in media of constant composition or of constant D.

5. The entropy of activation is likewise dependent upon T, D and μ when determined in media of constant composition, but is independent of T and D when determined in isodielectric media, in agreement with theoretical equations developed by La Mer.

6. The energy of activation of the reaction freed from the electrostatic net charge contributions has been determined through the Arrhenius equation employing isodielectric solvents at different temperatures.

7. The entropy of activation of an ionic reaction when D is held constant is identical—except for a very small and calculable ion atmosphere effect—with that for electrically uncharged molecules of the same chemical characteristics. This treatment permits direct comparison with the predictions of the collision theory, with which this reaction is in satisfactory agreement.

8. The electrostatic contributions to the kinetics of this ionic reaction are determined chiefly by the dielectric constant of the medium and only to a minor extent by the specific solvent effect of ethyl and methyl alcohol.