Summary

The formation of four chlorinates of chloroform has been demonstrated during an investigation of the temperature–concentration relations of the system chloroform–chlorine:

(1) *chloroform hemichlorinate,* $(CHCl_3)_2\cdot Cl_2$ (m. p. −80.0°)
(2) *chloroform monochlorinate,* $CHCl_3\cdot Cl_2$ (m. p. −96.5°)
(3) *chloroform dichlorinate,* $CHCl_3\cdot 2Cl_2$ (m. p. −112.5°)
(4) *chloroform trichlorinate,* $CHCl_3\cdot 3Cl_2$ (m. p. −115°)

The five eutectic points are located, respectively, at −90, −102, −118, −121 and −123°.

On the assumption that one or more atoms of chlorine in the chloroform may act as donor to the free chlorine, tentative structural formulas for the chlorinates have been suggested.

Bromine forms no coördination compounds with chloroform. The eutectic point of the system chloroform–bromine is located at −72°.

ITHACA, N. Y. RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Temperature Dependence of the Energy of Activation in the Rearrangement of N-Chloroacetanilide

BY JOHN O. PERCIVAL AND VICTOR K. LA MER

Introduction

Until recently it has been an almost universal assumption to consider the energy of activation, defined as $E_{\text{act}} = RT^2(\text{d} \ln k/\text{d}T)$, as independent of the temperature. In 1933 La Mer[1,2] showed that Tolman's statistical development[3] demanded in general that E_{act} must be a function of temperature. He pointed out the importance of considering not only the energy but also the entropy and consequently the free energy of activation as concepts important for the interpretation of reaction velocity. A similar treatment involving a more explicit use of statistical formulas,[4,5] or the concept of an energy surface[6] for the calculation of the properties of the state and the reactivity of the intermediate complex for gaseous reactions[7] has proved useful in the hands of the authors cited.[8]

The reluctance in many quarters toward accepting E_{act} as a function of temperature arises from the fact that the precision obtainable in the study of the kinetics of gaseous reactions is rarely sufficient to establish small variations. On the other hand, the situation is quite different for reactions in solution.

A reinvestigation of the depolymerization of diacetone alcohol in the presence of dilute sodium hydroxide has established that $\text{d}E_{\text{act}}/\text{d}T$ not only may be surprisingly large, but that E_{act} reaches a maximum at about 35°.[9]

Since further information regarding the behavior of the E_{act} for different types of reaction is of importance for the elucidation of chemical kinetics, we have studied the rearrangement of N-chloroacetanilide to C-chloroacetanilide in 0.2 molal hydrochloric acid, a reaction which requires simultaneous catalysis by H^+ and Cl^- ions. Harned and Seltz[10] found that E_{act} increases with temperature, but their E_{act} values do not agree with those which we calculate from Rivett's[11] earlier work, as shown in Fig. 1. The length of the arrows indicates the probable experimental error.

A preliminary study disclosed disturbing factors which had not been considered previously: *e. g.* (a) the possibility of interfering side reactions which might invalidate conclusions regarding E_{act}; (b) the unreliability of certified thermometers as temperature standards. We will present evidence that side reactions are insignificant, and will submit more precise values for E_{act} over a carefully selected set of temperatures, using an improved analytical technique.

Mechanism

The mechanism of the conversion has received

---

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

(2) V. K. La Mer, THIS JOURNAL, **55**, 1739 (1933).

(3) R. C. Tolman, "Statistical Mechanics," Chemical Catalog Co., New York, 1927, pp. 259–269.

(4) W. H. Rodebush, *J. Chem. Phys.*, **1**, 440 (1933).

(5) O. K. Rice and H. Gershinowitz, *ibid.*, **2**, 853 (1934).

(6) H. Eyring and N. Polanyi, *Z. physik. Chem.*, **12B**, 279 (1931).

(7) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935).

(8) Wynne-Jones and Eyring, *ibid.*, **3**, 492 (1935).

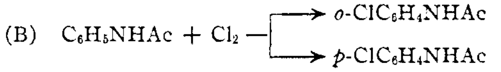
(9) V. K. La Mer and M. L. Miller, THIS JOURNAL, **57**, 2674 (1935).

(10) H. S. Harned and H. Seltz, *ibid.*, **44**, 1475 (1922).

(11) A. C. D. Rivett, *Z. physik. Chem.*, **82**, 201 (1913).

attention in Orton's laboratory.[12–16] In acetic acid solution, the reaction proceeds in two stages, the first of which is the rate determining step

$$\text{(A)}\quad C_6H_5NClAc + HCl \rightleftarrows C_6H_5NHAc + Cl_2$$



$$\text{(B)}\quad C_6H_5NHAc + Cl_2 \longrightarrow \begin{cases} o\text{-}ClC_6H_4NHAc \\ p\text{-}ClC_6H_4NHAc \end{cases}$$

N-Chlorinated anilides oxidize iodide ion to iodine while C-chlorinated anilides do not. The reaction is followed by titrating the iodine liberated with sodium thiosulfate when a sample is run into potassium iodide solution. Although direct proof is lacking, considerable circumstantial evidence exists to indicate that the above mechanism applies to aqueous solutions also.[14,16,17]

Blanksma[18] using 20% acetic acid as solvent and Rivett[11] using aqueous solutions found the rate of disappearance of the N-chloroacetanilide to be first order and proportional to the square of the hydrochloric acid concentration. Harned and Seltz[10] show for aqueous solutions that the observed rate is proportional to the activity of the hydrochloric acid

$$k = k_{\text{obsd.}}/a_{\text{HCl}} \qquad (1)$$

where $a_{\text{HCl}} = a_{\text{H}^+}\cdot a_{\text{Cl}^-} = a^2_\pm(\text{HCl}) = m^2f^2_\pm$ (a is thermodynamic activity, f is activity coefficient, m is molality).

Soper and Pryde[19] state that the observed rate is proportional not only to the activity of hydrochloric acid but also to the activity coefficient of the N-chloroacetanilide

$$k = k_{\text{obsd.}}/a_{\text{HCl}}f_{\text{:NCl}} \qquad (2)$$

and that the following interfering side reactions occur for which corrections should be made

$$\text{(C)}\quad C_6H_5NClAc + OH^- \rightleftarrows C_6H_5NHAc + OCl^-$$

$$\text{(D)}\quad ClC_6H_4NHAc + Cl_2 \longrightarrow ClC_6H_4NClAc + HCl^{20}$$

Pryde and Soper[19] conclude that (C) causes a 6% rate decrease in one tenth molar acid by a study of the rate of disappearance of N-chloroacetanilide in the presence of sulfuric, nitric, and chloric acids using phenol to remove hypochlorite. Soper[16] and Pryde and Soper[26] find the rate of hydrolysis in neutral solutions to be very small. We measured the hydrolysis at each temperature. It is only 0.1% of the rate of (A) in 0.2 molal hydrochloric acid.

It does not seem reasonable to suppose that the 6% decomposition of N-chloroacetanilide in acid solution was due to reaction (C), which is the reverse of the preparative reaction. Reaction (C) is analogous to (E)

$$\text{(E)}\quad Cl_2 + OH^- \rightleftarrows Cl^- + ClO^- + H^+$$

One would expect hydrogen ion to reverse both (C) and (E). Jakowkin[27] found this to be true for (E). Accordingly the effect they observe can be explained by (F) proposed by Rivett[11] where X is any acid anion

$$\text{(F)}\quad C_6H_5NClAc + HX \longrightarrow C_6H_4NXAc + HCl$$

followed by reaction (A) *et cetera*. Belton reports[28] instability of N-chloroacetanilide in sulfuric acid solutions even with no phenol present. Chattaway and Orton[29] have detected the formation of hydrochloric acid in solutions of N-chloroacetanilide in other acids. Soper[16] states that (D) causes a decrease in k of about 9% for 0.2 molal hydrochloric acid. If reaction (D) occurs, since its rate is a function of the concentration of the ortho and para chloroacetanilides, which increase with time by (B), the contribution of the N-chlorochloroacetanilide to the titer will become progressively greater causing k to drift downward.

However, since no time drift in k has been reported to date, nor detected in the present investigation after a careful search, we conclude that Soper's postulated side reaction (D) cannot occur to any perceptible extent.

Equation (2) of Soper and Pryde received experimental support from data making these two extensive corrections. Belton,[30] using NaCl–HCl mixtures and making no corrections, obtains data more satisfactorily explained by equation (1) than (2). For the present investigation, the reaction rates were obtained at constant activity of hydrochloric acid by equation (1).

---

(12) K. J. P. Orton, *Proc. Roy. Soc.*, **71**, 156 (1902).

(13) K. J. P. Orton and W. J. Jones, *J. Chem. Soc.*, **95**, 1456 (1909).

(14) F. S. Kipping, K. J. P. Orton, S. Ruhemann, A. Lapworth and W. J. Jones, Brit. Ass. Adv. Sci. Reports, 1910, p. 85.

(15) F. S. Kipping, K. J. P. Orton, S. Ruhemann, J. T. Hewitt and W. H. Grey, *Chem. News*, **108**, 155 (1913).

(16) F. G. Soper, *J. Phys. Chem.*, **31**, 1192 (1927).

(17) K. J. P. Orton and W. J. Jones, *J. Chem. Soc.*, **P25**, 233 (1909).

(18) M. J. J. Blanksma, *Proc. Akad. Sci. Amsterdam*, **5**, 178, 359 (1902); *Rec. trav. chim.*, **22**, 290 (1903); *ibid.*, **21**, 366 (1902).

(19) F. G. Soper and D. R. Pryde, *J. Chem. Soc.*, 2761 (1927).

(20) (B) and (D) have been studied in the following references: 13, 14, 16, 21, 22, 23, 24, 25; and (C) in 15, 16, 19; the rate of (B) is found (16) to be about one hundred times that of (D).

(21) K. J. P. Orton and H. King, *J. Chem. Soc.*, **99**, 1369 (1911).

(22) K. J. P. Orton and A. E. Bradfield, *ibid.*, 986 (1927).

(23) K. J. P. Orton, F. G. Soper and G. Williams, *ibid.*, 998 (1928).

(24) G. Williams, *ibid.*, 37 (1930).

(25) D. R. Pryde and F. G. Soper, *ibid.*, 1510 (1931).

(26) D. R. Pryde and F. G. Soper, *ibid.*, 1514 (1931).

(27) A. A. Jakowkin, *Z. physik. Chem.*, **29**, 613 (1899).

(28) J. W. Belton, *Proc. Leeds Phil. Lit. Soc.*, **2**, 178 (1931).

(29) F. D. Chattaway and K. J. P. Orton, *Proc. Chem. Soc.*, **18**, 200 (1902).

(30) J. W. Belton, *J. Chem. Soc.*, 116 (1930).

The above considerations show that the rate of disappearance of N-chloroacetanilide catalyzed by hydrochloric acid may be followed through its reaction with iodide ion without interfering side reactions and is suitable for a temperature coefficient study.

Precision Analysis

The important variables are: temperature (T), time (t), analyses for the concentration of the reacting compound (A, $A-x$), thermodynamic activity of the hydrochloric acid. The relation of these variables to E is shown in equations (1), (3) and (4)

$$E = \frac{RT_1T_2 \ln (k_2)/(k_1)}{T_2 - T_1} \tag{3}$$

$$k_{\text{obsd.}} = \frac{1}{t} \ln \frac{(A)}{(A - x)} \tag{4}$$

The influence of errors in determination of the variables on E was investigated by partial differentiation of these equations. The experimental procedure was then adjusted so that the combined effect of all calculable errors would be less than the effect of the uncertainty in the activity of hydrochloric acid given in the literature. Table I shows the effect of significant errors on k and E.

TABLE I

CALCULATED PROBABLE ERRORS

$e_{k(\ )} = \left(\frac{(10^2)}{k}\right)\left(\frac{\delta_k}{\delta(\ )}\right)\Delta(\ )$	%
$e_k(m)$	± 0.06
$e_k(f)$	± .12
$e_k(A)$	± .05
$e_k(A - x)$	± .05
$e_k(T)$	± .06
$e_k(t)$	± .01
$\Delta k = \sqrt{\Sigma(e_{k(\ )})^2}$	±16
$e_{E(\ )} = \frac{(10^2)}{E}\left(\frac{\delta_E}{\delta(\ )}\right)\Delta(\ )$	
$e_E(T)$	± .06
$e_E(k)$	± .38
$\Delta E = \sqrt{\Sigma(e_{E(\ )})^2}$	± .42
$\frac{\Delta E}{100} E$	±84.0 cal.

Experimental

The saturated solution of the compound was prepared by agitation *at the temperature of the run*[31]; a calculated amount was taken such that when mixed with the constant boiling hydrochloric acid, weighed out in a sealed thin glass capsule, would give a solution 0.2 *m* in hydrochloric acid. The reaction was terminated by pipetting samples into potassium iodide in the larger compartment of a special 125-cc. glass-stoppered Erlenmeyer flask[34] and by immediate mixing with a sodium hydroxide–sodium acetate solution contained in a side arm compartment. The final concentration of iodide was 4%[35]; the sodium hydroxide–sodium acetate was calculated to leave the solution at a *p*H of 5.75 ± 0.20.[36] This was verified by e. m. f. measurements using a glass electrode.

The liberated iodine was titrated with sodium thiosulfate from a weight buret using a starch indicator *within fifteen minutes* after taking the sample. The weight *in vacuo* of thiosulfate per gram of sample was substituted directly in equation (4). The precipitate formed during the reaction—of which no mention occurs in the literature—is excluded from the sample by drawing it through a sintered glass filter funnel. The extent of hydrolysis was determined by a second analysis of the saturated solution at the end of the experiment.

Preparation of the *N*-Chloroacetanilide.—The A solution was prepared according to directions of Barnes and Porter[37]; the remainder of the procedure was modified as follows. B solution, 9.6 g. of sodium hydroxide and 3.2 g. of sodium carbonate are dissolved in 150 cc. of solution. C solution, 1.9 g. potassium iodide in 37 cc. water; add 0.1 cc. of concentrated sulfuric acid immediately before addition of sample; add 2 cc. of 0.5% starch solution at the end-point. Chlorine is passed into B solution at 5° until 1 cc. added to C solution requires between 1.6/*M* and 1.8/*M* cc. of *M* molar thiosulfate. Add (220/*Mn*) cc. (*n* is the number of cc. of thiosulfate used) of solution B to solution A at 5°. Preserve the compound in a darkened vacuum desiccator over phosphorus pentoxide. If solution B is made from sodium carbonate only, the chlorine causes vigorous evolution of carbon dioxide which interferes with sampling.

Any method of recrystallizing involving heat treatment gave colored products with excessive melting point changes of from −10 to +70° due to decomposition. Addition of excess water at room temperature to an absolute alcohol solution was found to be the only satisfactory method of purification. The crystals were always white needles of reproducible m. p., 89.5°.

Temperature.—The temperature variation of the thermostats was ±0.005° or less. Baudin thermometer No. 18537 was used as a standard of temperature. The method of calibration leaves no doubt regarding the self-consistency of the scale.

The pipets were constructed from eight and twenty-four mm. Pyrex with no constriction of the tip to reduce errors of timing and heat losses in the fast runs. The main body was removed 4 to 5 cm. from the line of stems and was suspended in the thermostat before use long enough to reach temperature equilibrium. The pipets delivered 26 ± 2 cc. in less than two seconds, the exact value being determined by weight.

---

[31] The solution is customarily prepared by boiling several hours in water.[10,11] Porter and Wilbur,[32] and Bradfield[33] show that complete decomposition occurs within one-half to two hours at 100°.

[32] C. W. Porter and P. Wilbur, THIS JOURNAL, **49**, 2145 (1927)

[33] A. E. Bradfield, *J. Chem. Soc.*, 351 (1928).

[34] V. K. La Mer and M. E. Kamner, THIS JOURNAL, **57**, 2664 (1935); Fig. 1.

[35] R. M. Chapin, *J. Chem. Soc.*, **41**, 351 (1919).

[36] I. M. Kolthoff, I. H. Menzel and N. H. Furman, "Volumetric Analysis," John Wiley and Sons, New York, 1929, Vol. II, p. 354.

[37] C. D. Barnes and C. W. Porter, THIS JOURNAL, **52**, 1721 (1930)

Buffer.—A buffer is required for the following reasons. (a) Oxidation of iodide ion to iodine by dissolved oxygen will occur in the solution before the end-point is reached, unless the hydrochloric acid catalyst is neutralized. (b) Thiosulfate titrations[36] of dilute iodine require a definite acidity for quantitative results. (c) Hydrogen ion is needed for the reaction between the N-chloroacetanilide and iodide

$$C_6H_5NClAc + 2I^- + H^+ \longrightarrow C_6H_5NHAc + Cl^- + I_2$$

If N-chloroacetanilide is run into neutral potassium iodide, the *p*H rises to 10.75 and the reaction stops with only 60% of the compound reduced. Subsequent addition of acid will not yield the theoretical amount of iodine. (d) The fast running pipets used do not deliver reproducible quantities of solution (within ±2 cc.). The sodium acetate–sodium hydroxide mixture meets these requirements.

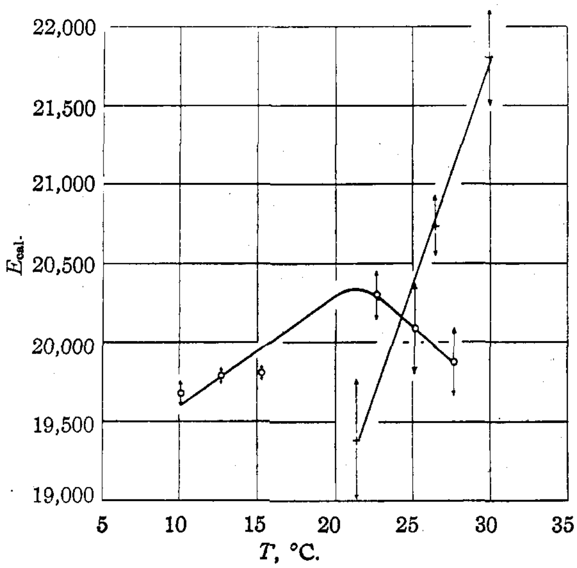


Fig. 1.—Energy of activation–temperature: +, Harned and Seltz; ○, Rivett.

Analysis.—The starch–iodine end-points are observed by holding the flask on a line with the eye and a lamp behind translucent glass in an otherwise light-tight box; the room is darkened. As the reaction progresses, the solution becomes slightly yellow so that successive end-points cannot be compared to obtain reproducibility. The solution is over-titrated with one drop of thiosulfate; a few cc. are placed in the side-arm and iodine added in 0.003-g. portions to the main body until the first perceptible difference in shade is observed between the two portions. This end-point is highly reproducible; when reaction products are present, it is red-yellow. A normality change of 1 × 10^{-6} is readily detected. The a. d. of four iodine–thiosulfate titrations was one-half this quantity. *Light.*—No difference was found on comparing runs in clear and blackened flasks. *Reagents.*—Eimer and Amend Technical Purity grade sodium thiosulfate was twice recrystallized between 60 and 5°. Approximately 0.02 *M* solutions were made in carbon dioxide-free water[38] which were kept free of carbon dioxide with soda-lime tubes. No decomposition of these solutions could be detected during the period of any run. Iodine was distilled from potassium iodide and copper sulfate[35] and sublimed three times. Potato starch ground for five hundred hours in a ball mill readily forms a suspension in water at room temperature. The blank for 2 cc. of a 0.5% solution is 2.1 × 10^{-7} equivalent of iodine. The constant boiling hydrochloric acid was prepared by the standard methods.[39,40]

TABLE II

k, E, B AT CONSTANT ACTIVITY HCl

T, °C.	k_{av}	Δk ± (%)	E_{act}	ΔE ± (%)	B	ΔB ± (%)
0.305	0.008550	0.79				
6.333			19170	1.36	13.23	1.5
12.362	.03792	.39				
12.645			19790	0.68	13.73	0.72
18.673			20440	.86	14.21	.91
18.925			20090	.49	13.96	.50
24.954			20590	.51	14.33	.56
24.984	.1742	.42				
31.264			20750	1.09	14.45	1.10
37.545	.7178	.52				

Calculation of Results

Values of k, E_{act} and B at constant activity of hydrochloric acid are shown in Table II with their experimental error. The errors represent the deviation between duplicate runs. k and E were calculated from (4), (1) and (3); B from (5).

$$B = \log k + (E_{act}/2.3\ RT) \qquad (5)$$

The activity coefficients were calculated to within ±0.0005 by the equation of Harned and Ehlers.[41] E_{act} and B are plotted against temperature in Figs. 2 and 3, respectively. The data of Rivett were recalculated to a molal basis. The E_{act} from Rivett, and Harned and Seltz were calculated using the activity coefficients of Harned and Ehlers[41] and are plotted in Fig. 1. The error in Rivett's data was calculated from the a. d. of a single run at each temperature. Harned and Seltz do not indicate whether they made duplicate runs, merely stating that "the maximum variation in a series was ±1%." This figure was used to calculate their ΔE. Our k values and those of Harned and Seltz agree at 25° to 3% when the latter are multiplied by 2.303. Time is in minutes.

Discussion

The increase of E from 19,170 to 20,750 cal. for the temperature range 6.333 to 31.264° corresponds to a mean molar heat capacity of activa-

---

[38] F. O. Rice, M. Kilpatrick and W. Lemkin, THIS JOURNAL, **45**, 1361 (1923).

[39] C. W. Foulk and M. Hollingsworth, *ibid.*, **45**, 1220 (1923).

[40] W. D. Bonner and A. C. Titus, *ibid.*, **52**, 633 (1930).

[41] H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 2179 (1933).

tion of 63 cal./deg. Figure 1 compared with Fig. 2 shows our data to give the most precise values of E. The change with temperature is unquestionably greater than experimental error, and cannot be due to side reactions nor to inconsistencies in the temperature scale used.

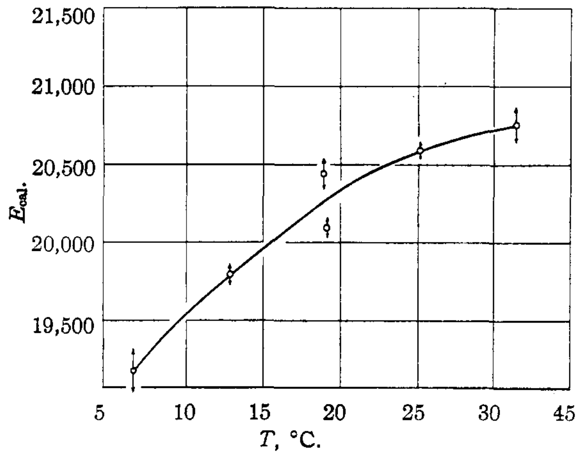


Fig. 2.—Energy of activation-temperature.

By integrating $\partial \ln k/\partial T = E_{\text{act}}/RT^2$ under the general assumption that $E_{\text{act}} = f(T)$, La Mer obtained

$$\ln k = \text{frequency constant} + (S_{\text{act}}/R) - (E_{\text{act}}/RT) \quad (6)$$

where S_{act} is the entropy of activation. When E_{act} is considered independent of temperature, S_{act}/R vanishes, since it is equal to

$$\frac{1}{R}\int_0^T \left(\frac{\partial E_{\text{act}}}{\partial T}\right) \mathrm{d}T/T$$

He evaluated the constant of integration by assuming a collisional mechanism for the reaction, in which case the frequency term = $\ln Z°$. Comparison of eq. (5) with eq. (6) shows that for this mechanism

$$B = \log Z° + S_{\text{act}}/2.3R \quad (7)$$

The experimental value of B, equal to 13.23 at 6.33°, compares favorably with the value of $\log Z°$ equal to 13.10, assuming σ equal to 5A°. However at 31.26° B has increased 1.22 units. whereas $\log Z°$, which varies as $T^{1/2}$ has increased but 0.02 unit. This constitutes further experimental proof of the existence of an appreciable entropy of activation. The simple collision theory of reaction kinetics obviously is quite inadequate.

Eyring has proposed a statistical theory which avoids the collisional mechanism for evaluating the frequency constant in eq (6). His theory yields

$$B = \log \kappa kT/h + S_{\text{act}}/2.3R \quad (8)$$

Here kT/h is a universal frequency which varies as T; κ is a transmission coefficient representing the probability that the activated complex will not be reflected back after passing the energy barrier. Calculations of κ are not available except for extremely simple reactions.

The entropy of activation in (7) differs from that in (8) in that the collisional mechanism for the process $A + B \rightleftarrows X$ apportions the entropy contribution associated with the ordinary translational degrees of freedom of A, B and X to $Z°$, whereas in eq. (8) these contributions are included under S_{act}.

It is of interest to note the striking similarity between the form of the curve, E_{act} *versus* T (Fig. 2), and that for the depolymerization of diacetone alcohol.[9] Our reaction involves a neutral molecule and two oppositely charged ions, while the latter reaction concerns a neutral molecule and one negative ion.

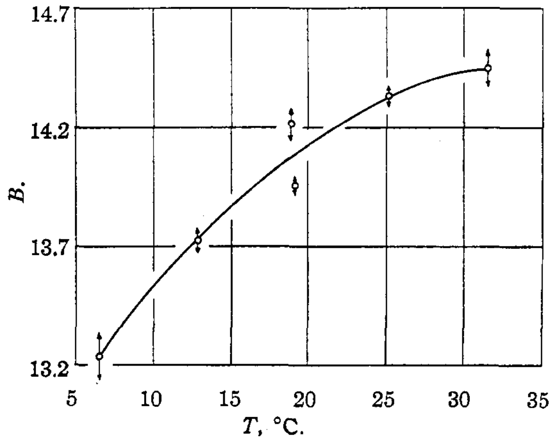


Fig. 3.—B-Temperature.

Summary and Conclusions

1. The rate of conversion of N-chloroacetanilide in the presence of aqueous 0.2 molal hydrochloric acid has been measured at 0, 12.5, 25, 37.5°. The temperature dependence of the energy of activation has been calculated for a constant activity of hydrochloric acid.

2. The analytical procedure has been refined so that the velocity constants can be reproduced to 0.5%.

3. The complete absence of time drifts of the velocity constant shows that the secondary N-chlorinations postulated recently by Soper do not exist.

4. The E_{act} rises steadily from 19,170 cal.

for the interval 0–12.5° to 20,750 cal. for 25–37.5°, corresponding to a mean heat capacity of activation of 63 cal./deg.

5. The form of the curve E *versus* T for this reaction is similar to that for the depolymerization of diacetone alcohol by hydroxyl ion.

6. The action constant B—which is equal to the entropy of activation plus a frequency term—varies from 13.2 at 6.33° to 14.45 at 31.3°. The magnitude and temperature dependence of B furnish additional evidence of the inadequacy of the collision theory, and of the existence of an appreciable entropy of activation.

NEW YORK, N. Y. RECEIVED AUGUST 24, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Orthobaric Densities of Substances as a Function of Reduced Temperatures

BY HAROLD A. FALES AND CLARA S. SHAPIRO

In the present investigation it is our purpose to make a comparative study of the equilibrium between the liquid and vapor phases of different elements and chemical compounds over the entire range of coexistence of the two phases from the melting point to the critical temperature with particular reference to the relationship between the orthobaric densities and the "reduced" temperatures.

Cailletet and Mathias studied the densities of the liquid and gaseous phases and discovered in 1886[1] that the arithmetical mean of their sum is a function of centigrade temperature. Likewise, they found that the "reduced" mean density can be expressed as a function of "reduced" temperature; this relationship is discussed in detail by Van Laar.[2] Recently two interesting papers have appeared along the lines of our subject. One is by C. H. Meyers[3] in which orthobaric volumes are connected with "reduced" pressures and absolute temperatures. This author shows for twenty-three substances that provided the vapor pressure–temperature relation for the saturated fluid, the critical pressure, and approximate values for liquid densities are known, the specific volume of the saturated vapor can be calculated, except near the critical temperature, with the determination of one empirical constant in the equation

$$\log_{10}\left(1-\frac{pv}{RT}\right)\left(1-\frac{pv'}{RT}\right) = A\log_{10}\frac{p}{2.718p_c} \qquad (1)$$

where p = saturation pressure, p_c = critical pressure, v and v' = specific volumes of liquid and vapor respectively, R = gas constant, T = absolute temperature and A = empirical constant which varies slightly from 0.72 for noble gases to 0.61 for methanol, with an average value of 0.69 for twenty-three substances. The above relationship is very accurate up to one-fourth to one-half the critical pressure, which corresponds to 0.8 to 0.9 the absolute critical temperature.

The second paper is by J. Horiuchi[4] and deals with the expression $\ln v_g/v_l$. Assuming that Maxwell's distribution law and van der Waals' equation apply to the equilibrium liquid $\rightleftarrows$ saturated vapor, and introducing a certain correction Horiuchi develops an equation which expresses $\ln v_g/v_l$ in terms of two variables: the volumes themselves and the absolute temperatures, namely

$$\ln v_g/v_l = \frac{A}{RT}\left(\frac{1}{v_l - E} - \frac{1}{v_g - E}\right) \qquad (2)$$

where A and E are constants characteristic for each substance. This equation holds well for a large number (60) of organic and inorganic liquids up to 0.8–0.9 of the critical temperature. It deviates considerably in the case of methyl alcohol and does not hold at all for water; according to Horiuchi this discrepancy is due to the strong association of these liquids. As to constants A and E they differ in numerical value for different substances. For normal organic liquids $A = 32.3\ T_{cr}^2/P_{cr}$ and $E = 0.17\ V_{cr}$, so that a "reduced" equation is obtained for these liquids[4]

$$\ln\frac{\phi_g}{\phi_l} = \frac{1.47}{R\tau}\left(\frac{1}{\phi_l - 0.17} - \frac{1}{\phi_g - 0.17}\right) \qquad (3)$$

where τ, ϕ_g, ϕ_l are the reduced temperatures and reduced volumes, respectively.

The expression $\ln v_g/v_l$ has previously received considerable attention in the literature, mostly in

---

(1) Cailletet and Mathias, *Compt. rend.*, **102**, 1202 (1886); **104**, 1563 (1887); Mathias, *ibid.*, **200**, 1643 (1935); **200**, 1902 (1935).

(2) Van Laar, "Zustandgleichung," ed. 1924, pp. 74, 342–350.

(3) C. H. Meyers, *Bur. Standards J. Research*, **11**, 691 (1933).

(4) J. Horiuchi, *Bull. Chem. Soc. Japan*, **1**, 189 (1926); and **2**, 213 (1927). *Sci. Papers, Inst. Phys. Chem. Research, Tokyo*, **15**, 89 (1931).