for the formation of both types of complex; the naphthalene ring provides a site for π-π bonding and the nitrogen of the pyrroline possesses an electron which can be donated to an accepting orbital of a nitro group to form an n-π bond. Because of steric factors, a single donor molecule will probably have only one picric acid molecule associated with it, either in a π-π or an n-π bond.

2,3-Diaminobutane Picrate (No. 40).—In the spectrum of the 2,3-diaminobutane–picric acid complex, the pronounced shift of the NH_2 stretching vibrations to lower frequencies (3420 to 3207 cm.$^{-1}$) clearly indicates that the product is stabilized by hydrogen bonds between the amino hydrogens of one component and the nitro oxygens of the other. There are other cases where hydrogen bonding may further stabilize already formed π-π and n-π complexes, as in the picrates of aniline, β-naphthylamine and piperidine.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Application of Differential Thermal Analysis to the Study of Reaction Kinetics[1]

BY HANS J. BORCHARDT AND FARRINGTON DANIELS

RECEIVED JULY 23, 1956

Equations are derived which relate the shape of a differential thermal analysis curve to the kinetics of the reaction giving rise to the curve. For certain reactions, use of these equations allows the order of the reaction, the frequency factor, the activation energy and the heat of reaction to be determined in a single rapid measurement. The equations are applied to the decomposition of benzenediazonium chloride and the reaction between dimethylaniline and ethyl iodide. The results agree very well with data obtained by conventional methods.

Increasing use has been made of differential thermal analysis (DTA) in recent years for studying the processes which a substance undergoes on heating.[2] The differential thermograph is commonly used to determine if a reaction or transition occurs and the temperature at which it takes place. The present article shows that the kinetic parameters for the reaction giving rise to the DTA curve can be accurately determined by an analysis of the shape (*i.e.*, slope, height, area) of the curve. Conditions are assumed in the derivation which can be met more readily by liquids than by solids. The present discussion will therefore concern itself primarily with reactions occurring in solution.

Theory

The apparatus referred to in this derivation is shown in Fig. 1. It consists of two cells mounted in a bath. One cell contains the solution of reactants and the other pure solvent or other inert liquid. The contents of the cells are agitated by the indicated stirrers. The temperature of the bath is raised by a heater (not shown). The temperature of the reactant solution as well as the temperature difference between the contents of the two cells (ΔT) is measured as a function of time. A differential thermocouple (DTC) may be used to measure ΔT. The run is started at a sufficiently low temperature so that the reaction is not occurring at an appreciable rate and it is carried through until the reaction has gone essentially to completion. A curve such as the one in Fig. 2 is obtained.

T_1, T_2 and T_3 are the temperatures of the reactant solution, the liquid in the reference cell and the bath, respectively. $C_{p,r}$ is the total heat capacity of the reactant solution and $C_{p,s}$ the total heat capacity of the liquid in the reference cell.

We first set up the equations of heat balance (eq. 1 and 2). Equation 1 states that the increase in the enthalpy of the reactant solution ($C_{p,r}\,dT_1$) is equal to the heat evolved by the reaction (dH) plus the heat transferred into the cell from the surroundings.

$$C_{p,r}\,dT_1 = dH + K_r\,(T_3 - T_1)dt \qquad (1)$$

K_r is the heat transfer coefficient of the reactant cell and dt the time interval. Similarly for the liquid in the reference cell we have

$$C_{p,s}\,dT_2 = K_s\,(T_3 - T_2)dt \qquad (2)$$

where K_s is the heat transfer coefficient of the reference cell.

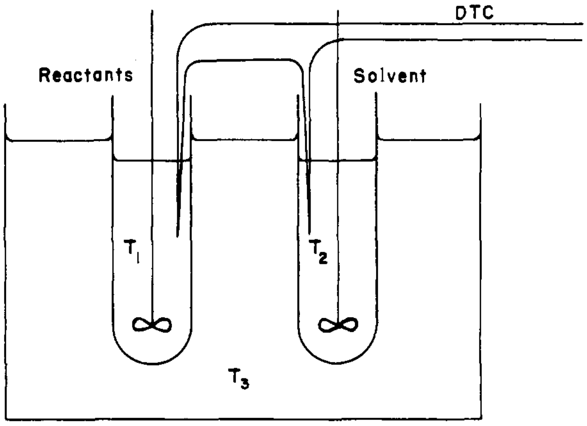

Fig. 1.—DTA apparatus for obtaining kinetic data for reactions occurring in solution.

Thus far two assumptions have been made. The first is that the temperature in the respective cells is uniform. This assumption was made when a single value of the temperature (T_1 and T_2) was assigned to the liquids in the cell. The condition

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[1] Presented in part at the 129th meeting of the American Chemical Society, Dallas, Texas, April, 1956. Further details may be found in a Ph.D. thesis by Hans J. Borchardt, filed with the Library of the University of Wisconsin, June, 1956.

[2] For an introduction to differential thermal analysis see H. J. Borchardt, *J. Chem. Ed.*, **33**, 103 (1956).

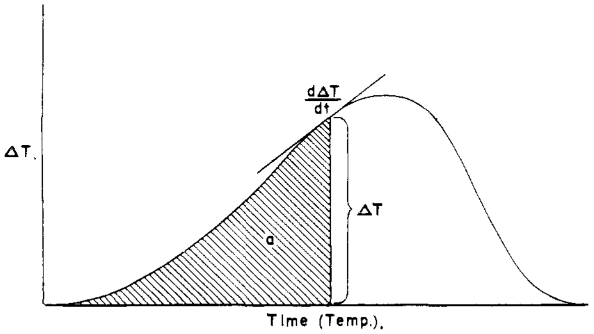

Fig. 2.—DTA curve showing the quantities which are measured in order to evaluate the rate constants for the reaction giving rise to the curve.

of uniform temperature cannot be met exactly by solids, but can be met by liquids which are stirred. It was for this reason that these considerations were limited to reactions in solution. The other assumption is that heat is transferred by conduction alone. This assumption is valid in the temperature range where one would usually be working with solutions. Heat transfer through the thermocouple wires is neglected.

At this point two additional conditions are assumed. One is that $K_r = K_s = K$. The heat transfer coefficients will be equal if identical cells are used and if they are filled to the same level. We therefore drop the subscript and characterize these cell constants by a single symbol K. The other assumption is that $C_{p,r} = C_{p,s} = C_p$. The heat capacities of the two liquids will be nearly the same if the reactant solution is dilute and if pure solvent is used as the reference liquid. If the reaction involves several components, a solution containing all but one of the reactants (so that no reaction can take place) would approximate closely the heat capacity of the reactant solution and serve well as the reference liquid. Because the cells must be filled to the same level, the volumes of the two liquids are the same; hence the heat capacities per unit volume should match. This is fortunate since the heat capacities of solutions and solvents are often nearly the same on a volume basis.

Since the subscripts on C_p and K have been dropped, eq. 2 may be subtracted from eq. 1 giving

$$\mathrm{d}H = C_p\,\mathrm{d}\Delta T + K\Delta T\,\mathrm{d}t \qquad (3)$$

where the conventional symbol ΔT has been substituted for $T_1 - T_2$. In order to obtain an expression for the total heat transferred, eq. 3 is integrated between $t = 0$ and $t = \infty$. Assuming C_p and K to be independent of temperature (time) over the interval where the reaction occurs, we obtain

$$\Delta H = C_p(\Delta T_\infty - \Delta T_0) + K\int_0^\infty \Delta T\,\mathrm{d}t \qquad (4)$$

Since ΔT is zero at both $t = 0$ and $t = \infty$ (see Fig. 2), the first term is just zero. The integral is the total area under the curve (A). Therefore

$$\Delta H = KA \qquad (5)$$

This equation which states that the area under the DTA curve is directly proportional to the heat transferred in the reaction was first derived by Spiel[3] in a somewhat different manner. Since ΔH is the total heat transferred, the heat of reaction per mole is given by KA/n_0 where n_0 is the initial number of moles of reactant.

It is now assumed that the heat evolved in a small time interval is directly proportional to the number of moles reacting during that time.

$$\mathrm{d}H \propto -\mathrm{d}n;\ \mathrm{d}H = -\frac{KA}{n_0}\,\mathrm{d}n \qquad (6)$$

The constant of proportionality is clearly the heat of reaction per mole. Here the heat of reaction is assumed to be constant over the temperature interval where the reaction occurs. Substituting eq. 6 for $\mathrm{d}H$ in eq. 3 and differentiating with respect to time gives

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{n_0}{KA}\left[C_p\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + K\Delta T\right] \qquad (7)$$

This equation gives the actual rate of reaction at any temperature in terms of the slope ($\mathrm{d}\Delta T/\mathrm{d}t$) and height ($\Delta T$) of the curve at that temperature.

The number of moles present (n) at any instant is equal of the initial number of moles (n_0) minus the number of moles that have reacted.

$$n = n_0 - \int_0^t -\frac{\mathrm{d}n}{\mathrm{d}t}\,\mathrm{d}t \qquad (8)$$

Substituting into eq. 8 the expression for the rate of reaction (eq. 7) gives

$$n = n_0 - \frac{n_0}{KA}\left[C_p\int_0^t \frac{\mathrm{d}\Delta T}{\mathrm{d}t}\,\mathrm{d}t + K\int_0^t \Delta T\,\mathrm{d}t\right] \qquad (9)$$

Integrating

$$n = n_0 - \frac{n_0}{KA}[C_p\,\Delta T + Ka] \qquad (10)$$

The second integral in eq. 9 is the area that has been swept out (a) at time t. The quantity a is shown in Fig. 2.

The expression for the rate constant of a reaction of order x with respect to one component is

$$k = -V^{x-1}\frac{\mathrm{d}n/\mathrm{d}t}{n^x} \qquad (11)$$

where V is the volume and n the number of moles (rather than concentrations). Substituting eq. 7 and 10 for $\mathrm{d}n/\mathrm{d}t$ and n, respectively, and rearranging gives

$$k = \left[\frac{KAV}{n_0}\right]^{x-1}\frac{C_p\dfrac{\mathrm{d}\Delta T}{\mathrm{d}t} + K\Delta T}{[K(A - a) - C_p\,\Delta T]^x} \qquad (12)$$

For the case of a first-order reaction ($x = 1$) eq. 12 simplifies to

$$k = \frac{C_p\dfrac{\mathrm{d}\Delta T}{\mathrm{d}t} + K\Delta T}{K(A - a) - C_p\,\Delta T} \qquad (13)$$

For the case of a reaction with respect to several components of the form $lL + mM + \cdots \rightarrow$ *products*, having the rate expression

$$\frac{\mathrm{d}z}{\mathrm{d}t} = (L - z)^l\left(M - \frac{m}{l}z\right)^m \qquad (14)$$

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[3] S. Spiel, Rept. Inv. No. 3765, Bur. of Mines, U. S. Dept. of Interior, 1944.

the equation becomes

$$k = \frac{\left[\frac{KAV}{L_0}\right]^{l+m-1}\left[C_{\mathrm{p}}\frac{\mathrm{d}\Delta T}{\mathrm{d}t} + K\Delta T\right]}{[K(A - a) - C_{\mathrm{p}}\,\Delta T]^{l}\left[K\left(\frac{M_0}{L_0}A - \frac{m}{l}a\right) - C_{\mathrm{p}}\,\Delta T\right]^{m}} \ldots \quad (15)$$

where z is the number of moles of L reacted in time t and L_0 and M_0 are the initial number of moles of L and M, respectively.

The various quantities are evaluated as follows.

K need only be evaluated once since it is a characteristic of the apparatus. It is best determined by means of eq. 5. A quantity of heat is dissipated in the cell either electrically or by carrying out a reaction where the heat effect is known. The ratio of heat evolved to the area under the resulting curve gives K. The dimensions of K are calories min.$^{-1}$ deg. C.$^{-1}$.

A is the total curve area. The dimensions are min. deg. C.

V/n_0 is the reciprocal of the initial concentration of reactants. If the volume changes considerably with temperature, this fact should be taken into consideration. The choice of units depends upon the dimensions in which the rate constant is desired.

C_{p} is the total heat capacity of the reactant solution or reference liquid. The heat capacities of most solutions are not well known. It will be shown in the experimental section that little error results if the value for the heat capacity of the solvent is used. The dimensions of C_{p} are cal. deg. C.$^{-1}$.

$\mathrm{d}\Delta T/\mathrm{d}t$, ΔT and a are the slope, height and area, respectively, of the curve at the temperature (time) at which k is being evaluated. The dimensions of these quantities are, respectively, deg. C. min.$^{-1}$, deg. C. and deg. C. min. The only term which remains is x (or $l + m$ in the case of eq. 14), the order of the reaction. If a value of x were assumed, k could be calculated at all temperatures over the range where the curve extends. The plot of ln k *versus* $1/T$ (activation energy plot) would yield a straight line if, and only if, the correct value of x had been assumed. It is this fact and procedure which is used to determine the order of the reaction. One varies x, usually by integers, until the activation energy plot is linear. The value of x thus obtained is the order of the reaction.

The correct plot of ln k *versus* $1/T$ enables one, of course, to calculate the activation energy and frequency factor. Equation 5 gives the heat of reaction. The activation energy and the heat of reaction enable one to calculate the activation energy for the reverse reaction.

These equations assume that the reaction is carried out at constant pressure. Analogous equations are obtained for constant volume. Here C_{v} replaces C_{p}, and ΔE, the change of internal energy, replaces ΔH.

These considerations may also be applied to differential enthalpic analysis (DEA). In this method, the temperature difference between the active and reference material is maintained at zero by supplying heat to either the active or reference materials during a reaction. Thus $\mathrm{d}H/\mathrm{d}t$ is measured and plotted directly as a function of time (temperature). This approach has been pursued by Eyraud.[4] In this case the total area is equal to the heat transferred

$$\Delta H = A \quad (16)$$

If it is assumed that the heat evolved is directly proportional to the number of moles reacted, it follows that

$$-\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{n_0}{A}\frac{\mathrm{d}H}{\mathrm{d}t} \quad (17)$$

An expression for the amount of reactant present at any instant is obtained in the same manner as before.

$$n = n_0 - \frac{n_0 a}{A} \quad (18)$$

Thus the rate constant is given by

$$k = \frac{\left(\frac{AV}{n_0}\right)^{x-1}\frac{\mathrm{d}H}{\mathrm{d}t}}{(A - a)^{x}} \quad (19)$$

Equation 19 is not limited to differential enthalpic analysis. It would apply to any procedure where the rate of change of a physical property, proportional to the rate of reaction, is measured as a function of temperature and time under conditions where the temperature is changing. The physical property should be nearly independent of temperature. A different proportionality constant would appear in eq. 17 and 19 if the physical property was other than the heat transferred during a reaction.

Discussion of Assumptions.—The following list summarizes the assumptions made in the derivation of the equations for DTA and the conditions which must practically be met; (1) The rate of reaction is very small at the lowest temperature practically obtainable; (2) the reaction goes essentially to completion before the highest obtainable temperature is reached; (3) the reaction must be accompanied by a measurable heat effect; (4) the temperature in the cells is uniform; (5) heat is transferred to the solutions by conduction alone; (6) $K_{\mathrm{r}} = K_{\mathrm{s}}$; (7) $C_{\mathrm{p,r}} = C_{\mathrm{p,s}}$; (8) C_{p}, K and ΔH do not vary over the temperature interval where the reaction occurs; (9) no heat is transferred through the thermocouples; (10) dn is proportional to dH; (11) the kinetics of the reaction can be described by a single rate constant; (12) the activation energy does not vary with temperature.

Assumptions 4, 5, 6 and 7 have been discussed. It will be shown in the Experimental section that inequalities in the cell constants and heat capacities have little effect on the results. Assumptions 8 and 12 are met almost exactly for temperature intervals that one might encounter in normal solution studies. Heat transfer through the thermocouple is taken account of for all practical purposes, when the cells are calibrated. Assumptions 10 and 11 restrict the method to reactions which meet these conditions experimentally. Thus complex reactions are generally excluded. Some simple reaction which produces a gaseous product may not meet condition 10. If the gas forms a non-ideal solution with the solvent and exceeds its solubility in the

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[4] C. Eyraud, *Compt. rend.*, **238**, 1511 (1954).

course of the reaction, an interfering heat effect may occur. This problem may be overcome in some instances by working at constant volume rather than constant pressure. Assumptions 1 and 2 are essentially restrictions on the solvent. The freezing and boiling points of the solution should be such that the DTA curve occurs well within these temperatures. Problems due to vaporization of solvent may be overcome by conducting the experiments at constant volume. With regard to assumption 3, reactions accompanied by a heat transfer of 5 kcal./mole can be quantitatively studied with the simple apparatus described below. Improved instrumentation could probably lower this limit.

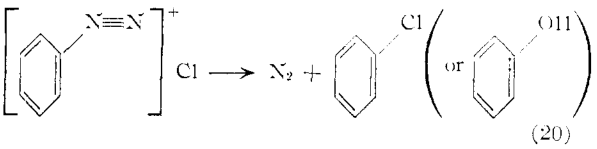
Experimental

Apparatus.—The cells consist of two Pyrex tubes, 1.25 inches in diameter and 5 inches long. They have a capacity of about 60 ml. The differential thermocouple (DTC) is a 0.028 inch o.d. copper tube with a coaxial constantan wire, insulated from the copper by fiberglass. This type of thermocouple is available from the Precision Tube Company, North Wales, Pa. under the trade name, Coaxitube. The thermocouples were coated with Kel-F to protect them from being attacked by the reactants. The bath temperature is raised by a conventional heater controlled by a Variac. It should be noted that a linear temperature rise is not required. The output from the thermocouple runs to a Liston-Becker Model 14 d.c. breaker amplifier. From here the signal goes to a Brown recording potentiometer having a scale 0-20 mv. A fine-scale chart paper having 20 divisions/inch is used. The bath temperature (T_3) is measured with a calibrated mercury thermometer which can be read directly to 0.1°.

It was assumed that the temperature difference between the bath and reactant solution was negligible within the limits required for activation energy calculations, hence the bath temperature was used for this calculation.

Calibration.—The heat of dilution of H_2SO_4 was used to determine K. One ml. of $H_2SO_4 \cdot 4.964H_2O$ was added to 35 ml. of water in the reaction cell. This dilution is accompanied by the evolution of 32.21 cal. of heat.[5] A curve having an area of 3.72 sq. inches resulted. This gives K as 8.66 cal./in.². A chart speed of $^1/_2$ in./min. was used throughout. It was further found that a ΔT of 1° caused a pen displacement on the recorder of 8.95 in. With these two conversion factors, K becomes 38.8 cal./min. °C. The conversion factor for ΔT from inches to degrees was determined by sending a 30 microvolts signal into the amplifier. The observed pen displacement of 6.61 in. together with the known e.m.f. of the copper-constantan couple (40.6 microvolts/°C.) gives the figure of 8.95 in./°C.

Reactions.—The thermal decomposition of benzenediazonium chloride has been studied by Crossley, Kienle and Benbrook[6] who found the reaction to be first order with an activation energy of 27.2 kcal./mole and a frequency factor of $10^{15.2}$ sec.$^{-1}$. The reaction is



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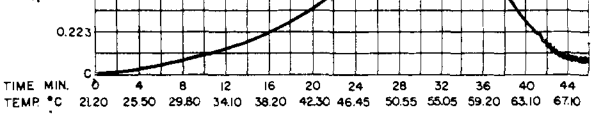

Fig. 3.—DTA curve for the decomposition of benzenediazonium chloride. Temperature difference between the reactant solution and inert liquid is plotted as a function of temperature and time.

The products are nitrogen and chlorobenzene or phenol or both, depending upon the conditions.[7] Benzenediazonium chloride was synthesized after the method described by the above authors. Thirty-five ml. of a 0.4 M aqueous solution was inserted into one cell and 35 ml. of distilled water into the other. The initial bath temperature was 2°. The bath temperature was raised at a rate of approximately 1°/min. The reaction is exothermic. The resulting curve is shown in Fig. 3. This figure shows that the curve did not return exactly to $\Delta T = 0$ at the conclusion of the reaction. For the purpose of the calculations, the baseline was taken to be the slanted line joining the curve extremities. In order to obtain data for the activation energy plot, the height, slope and area of the curve were measured at 7 temperatures. The rate constant was calculated at these temperatures from eq. 13. The data are given in Table I.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF BENZENEDIAZONIUM CHLORIDE

Temp., °C.	k, sec.$^{-1}$	Temp., °C.	k, sec.$^{-1}$
35	1.82×10^{-4}	54	2.74×10^{-3}
40	3.85×10^{-4}	57	4.00×10^{-3}
45	7.90×10^{-4}	61.2	7.38×10^{-3}
50	1.64×10^{-3}		

Figure 4 shows the first-order activation energy plot and a comparison with the data of Crossley and co-workers.[6] It may be noted that the best straight line through Crossley's points has a slightly lower slope than the line through the DTA points. Thus, the activation energies do not agree exactly. By DTA one obtains an activation energy of 28.3 kcal./mole and a frequency factor of $10^{16.3}$ sec.$^{-1}$. From eq. 5 the heat of reaction is found to be −37.0 kcal./mole. This gives 28.3 − (−37.0) = 65.3 kcal./mole as the activation energy for the reverse reaction. Two other runs were performed to determine the reproducibility of the results. Activation energies of 28.3, 29.1 and 28.5 kcal./mole were obtained.

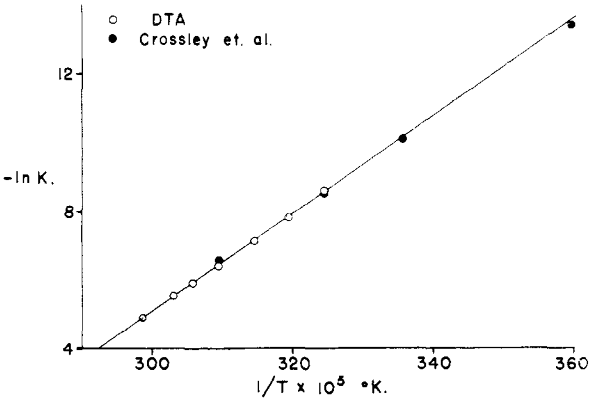

Fig. 4.—Activation energy plot for the decomposition of benzenediazonium chloride. The circles represent the data obtained by differential thermal analysis (DTA) and the solid points the data of Crossley and co-workers.[6]

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[5] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards Cir. 500, 1952, pp. 42-43.

[6] M. L. Crossley, R. H. Kienle and C. H. Benbrook, THIS JOURNAL, **62**, 1400 (1940).

[7] The formation of both chlorobenzene and phenol in the decomposition of benzenediazonium chloride makes this a complex reaction. The fact that good agreement is obtained suggests that the heats of formation of chlorobenzene and phenol do not differ greatly.

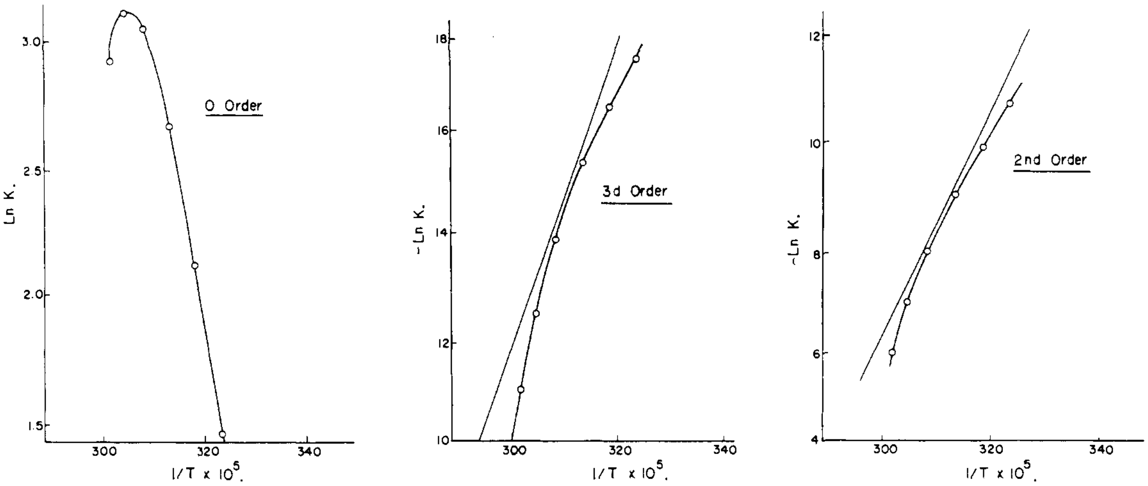
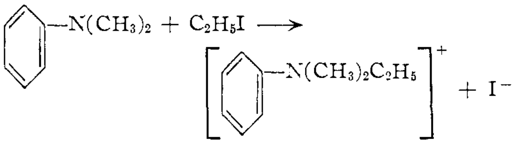


Fig. 5.—Activation energy plots for the benzenediazonium chloride decomposition assuming the order of the reaction to be zero, second, and third.

In order to test the validity of the procedure for determining the order of the reaction, *k* was recalculated assuming the orders to be zero, second and third, respectively. The plots are shown in Fig. 5. Distinctly non-linear curves result, verifying the procedure suggested. In this connection it may be pointed out that the data points in the first-order plot fit a straight line with an average deviation of only 0.18%.

The reaction of N,N-dimethylaniline with ethyl iodide to give N,N,N-dimethylethylanilinium iodide is discussed by Moelwyn-Hughes.[8] The reaction is



It is a bimolecular reaction, but if dimethylaniline is used as solvent and is accordingly in large excess, the reaction follows pseudo first-order kinetics. The activation energy and frequency factor are 14.0 kcal./mole and $10^{5.12}$ sec.$^{-1}$, respectively.[8] Since these values for the kinetic parameters are considerably different from those of the benzenediazonium chloride decomposition, it seemed an appropriate reaction to study.

Thirty-five ml. of dimethylaniline was inserted into the reactant cell and 40 ml. into the reference cell. When thermal equilibrium was established, 5 ml. of ethyl iodide was added to the reactant cell. The run was started at 25° and terminated at 150°. The resulting curve extended from 45 to 140°, the maximum occurring at 117.5°. The rate of temperature rise was approximately 2.3°/min. The time-interval was 40 minutes. Inasmuch as the reaction is first order,[8] rate constants were calculated at seven temperatures from eq. 13. The values are given in Table II.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE REACTION BETWEEN N,N-DIMETHYLANILINE AND ETHYL IODIDE

Temp., °C.	*k*, sec.$^{-1}$	Temp., °C.	*k*, sec.$^{-1}$
84.6	3.16×10^{-4}	111	1.96×10^{-3}
91.2	4.51×10^{-4}	117	3.66×10^{-3}
98.0	7.39×10^{-4}	125	5.55×10^{-3}
104.5	1.27×10^{-3}		

The activation energy plot is shown in Fig. 6. The straight line is based on the activation energy of 14.0 kcal./mole and frequency factor of $10^{5.12}$ sec.$^{-1}$, quoted by Moelwyn-Hughes.[8] The circles represent the data obtained by DTA.

Some experimental difficulties were encountered with the present apparatus at elevated temperatures. There was considerable vibration in the recorder pen at temperatures above 70°. This accounts for the presence of more scatter in the points on the activation energy plot. On the basis of the total curve area, the heat of reaction was found to be −20.4 kcal./mole. This gives 34.4 kcal./mole as the activation energy for the reverse reaction.

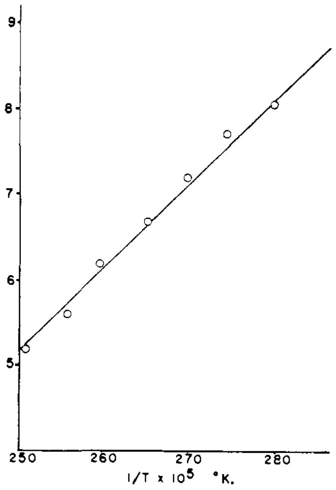


Fig. 6.—Activation energy plot for the reaction between N,N-dimethylaniline and ethyl iodide.

Discussion

It is interesting to note the order of magnitude of the quantities in eq. 13. For the benzenediazonium chloride decomposition, $C_p d\Delta T/dt$ varies from 0.634 at 35° to −2.70 at 61.2°. $K\Delta T$ over this range varies from 4.67 to 13.1 going through a maximum of 28.1 at 54°. $K(A - a)$ varies from 486 to 25.5 and $C_p\Delta T$ from 4.22 to 11.83 having a maximum of 25.4 at 54°. It is thus apparent that the quantities ($C_p\, d\Delta T/dt$) and $C_p\Delta T$ are usually an order of magnitude smaller than the quantities to which they are added and subtracted. Neglecting these smaller terms, eq. 13 becomes

$$k = \frac{\Delta T}{A - a} \tag{21}$$

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[8] E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solution," Oxford, 1933, p. 42.

and eq. 12

$$k = \frac{\left[\frac{AV}{n_0}\right]^{x-1} \Delta T}{(A - a)^x} \qquad (22)$$

These equations clearly indicate why this method is so insensitive to errors. The heat capacity essentially drops out. Slopes, which cannot be accurately measured have only a small effect on the final equation. The cell constant also tends to cancel out. The dominating terms in the equation are the height (ΔT) and remaining area of the curve ($A - a$), both of which can be measured accurately. In view of this fact, one would tend to assign more significance to the points calculated at lower temperatures where the remaining area is large and less susceptible to errors and where the smaller terms have the least influence.

It should be noted that eq. 22 is identical to eq. 19, the rate constant expression in differential enthalpic analysis. This demonstrates that the curves obtained by DTA and DEA are to a good degree of approximation the same.

The exceptional feature of this approach to kinetics is the rapidity with which the measurements are performed. The complete procedure including analysis of the data requires about one day, where a conventional approach may require several weeks to obtain the same data.

Acknowledgment.—The support of the U. S. Rubber Company in granting one of the authors (HJB) a fellowship is acknowledged with thanks.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF ILLINOIS INSTITUTE OF TECHNOLOGY AND THE UNIVERSITY OF MICHIGAN]

The Thermal Decomposition of Chloroform. II. Kinetics[1a]

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RECEIVED JUNE 19, 1956

The kinetics of the thermal decomposition of gaseous chloroform and chloroform-*d* have been investigated from 450–525°. At low extent of reaction the rate expression was found to be $-\mathrm{d}/\mathrm{d}t\,[\mathrm{CCl_3H}] = k[\mathrm{CCl_3H}]/(1 + b[\mathrm{HCl}])^{1/2}$. The activation energy based on initial slopes was 37.2 ± 2.0 kcal./mole for chloroform and 37.5 ± 2.0 kcal./mole for chloroform-*d*. The frequency factor was 6.3×10^8 sec.$^{-1}$ in both cases. A mechanism satisfactory for low extent of reaction is (1) $\mathrm{CCl_3H} \rightarrow \mathrm{CCl_2H\cdot} + \mathrm{Cl\cdot}$; (2) $\mathrm{Cl\cdot} + \mathrm{CCl_3H} \rightleftharpoons \mathrm{HCl} + \mathrm{CCl_3}$; (3) $\mathrm{CCl_3\cdot} + \mathrm{Cl\cdot} \rightarrow \mathrm{CCl_4\cdot}$; (4) $\mathrm{CCl_3\cdot} \rightarrow \mathrm{CCl_2{:}} + \mathrm{Cl\cdot}$; (5) $\mathrm{CCl_2{:}} + \mathrm{CCl_3H} \rightarrow \mathrm{C_2Cl_4} + \mathrm{HCl}$. From the present data and auxiliary information in the literature the upper limit for the C–Cl bond dissociation energy in chloroform is estimated to be $E_1 \leq 72$ kcal./mole.

In Part I[2] the experimental methods were described and the distribution of products in the pyrolysis of chloroform was discussed. The results of the kinetic studies are reported here.

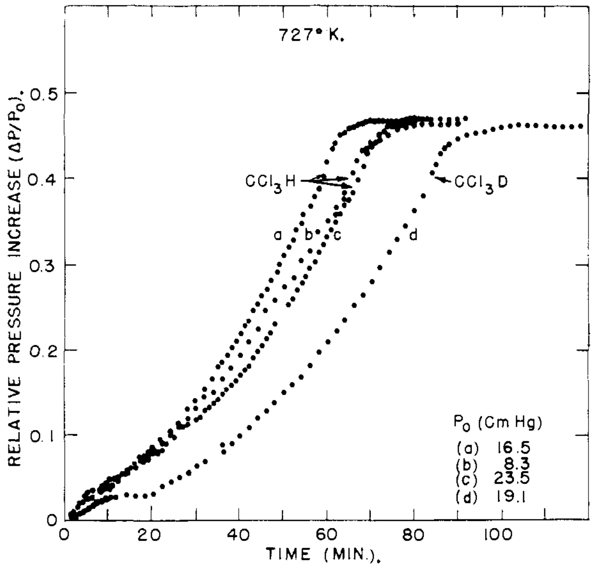

Fig. 1.—Pressure rise studies in static system.

Results and Discussion

A. Static System.—Figure 1 shows typical results of pressure-rise experiments carried out in the static system at 727 ± 2°K. The time for 25% pressure increase, "t_{25}," (very nearly equal to the half-time) showed no trend with initial pressure of chloroform. For five experiments with $P_0(\mathrm{CCl_3H})$ in the range 8–26 cm. t_{25} was 48 ± 2 min. This may be compared with the value $t_{25} = 24$ min. at 725°K. from the experiment of Verhoek.[3] Graphical differentiation of pressure-rise–time curves gave initial rates of about 3.5×10^{-3} min.$^{-1}$ which remained approximately first order in chloroform, in accord with Verhoek.[3]

For chloroform-*d*, the value of t_{25} was 66 min.; the average initial rate was about 2.5×10^{-3} min.$^{-1}$. More precise experiments using the flow system (as reported below) offered a much more reliable determination of the deuterium effect on the rate.

The reaction was found to be inhibited by hydrogen chloride. At 727°K., HCl ($P_0 = 7.4$ cm.) was added to $\mathrm{CCl_3H}$ ($P_0 = 21.1$ cm.); the resulting value of t_{25} was 75 min. Similar inhibition due to HCl was observed in the case of chloroform-*d*. The rate of pressure rise was, however, accelerated by added tetrachloroethylene (the major organic product), as discussed in Part I. For a run at 727°K. in which $\mathrm{C_2Cl_4}$ (2.8 cm.) was added to $\mathrm{CCl_3H}$ (16.6 cm.), t_{25} was 10 min.

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[1] (a) Part of a Ph.D. dissertation submitted by G.P.S. to the Graduate School of Illinois Institute of Technology; (b) Electrochemical Laboratories, Tulsa, Okla.

[2] G. P. Semeluk and R. B. Bernstein, THIS JOURNAL, **76**, 3793 (1954).

[3] F. H. Verhoek, *Trans. Faraday Soc.*, **31**, 1525 (1935).