walls will rise in a narrow tube. Yet Brunauer and co-workers[21] have gone to some length to discredit capillary condensation as an explanation of the higher portions of the isotherms. It may be needless to add that the formidable equation developed in this reference is based upon the same two errors.

It should be mentioned, however, that Emmett in his latest publication on the subject[22] has admitted the fact of capillary condensation although without clarification of its relationship to the equation developed.

The intention of these remarks is to emphasize the fact that the relation between sorption and surface area has not yet been adequately treated theoretically. It is hoped that others will take up the matter where it now stands and put it into more acceptable shape.

Summary

Sorption data on silica aerogel and silica xerogel are presented. It is shown that the area under the sorption curve, when plotted with log p_0/p as the abscissa, is a direct measure of the total surface area of the gel.

Capillary condensation is shown to influence greatly the course of all the curves studied, and in the case of non-aqueous liquids on silica gel may account for nearly all of the sorption measured.

Thorough removal of residual water from the surface of silica gel did not succeed in transforming the sorption curve to another type, as has been reported.

WORCESTER, MASS. RECEIVED SEPTEMBER 2, 1942

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[21] Brunauer, Deming, Deming and Teller, THIS JOURNAL, **62**, 1723 (1940).

[22] Emmett, "Advances in Colloid Science," Interscience Publishers, New York, N. Y., 1942, p. 1.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Kinetics of the Decomposition of Trinitrobenzoic Acid in Dioxane–Water Mixtures[1]

BY DAN TRIVICH[2] AND FRANK H. VERHOEK

In a previous paper[3] it was shown that the decomposition of 2,4,6-trinitrobenzoic acid in ethyl alcohol solution had as the rate-determining step the decomposition of the trinitrobenzoate ion. The decomposition proceeds at a faster rate in alcohol than in water, even though, as a result of the lower dielectric constant, the dissociation of the acid, and hence the concentration of the trinitrobenzoate ion, is smaller in the former solvent. Studies of the reaction in other solvents[4] have shown that the rate is dependent upon the solvent to a marked degree.

In order to secure further information concerning the effect of changes in solvent on this reaction, a study has been made of the decomposition of trinitrobenzoic acid in solvent mixtures of water and dioxane. The use of these two liquids permits a continuous variation in the composition of the solvent in a system for which the dielectric constant for each solvent mixture is known.[5]

The over-all reaction is a decarboxylation of trinitrobenzoic acid to form carbon dioxide and trinitrobenzene.

The rate of reaction was determined by keeping individual reaction flasks containing measured samples of solution at known temperatures, removing the flasks from the constant temperature baths after measured time intervals, and titrating with alkali the trinitrobenzoic acid remaining undecomposed.

Each solution was prepared by diluting a stock solution of trinitrobenzoic acid in pure dioxane with the proper amounts of water and dioxane to give the desired composition of solvent. Ten-ml. samples of the resulting solution were pipetted and placed in individual reaction vessels, which were covered and immersed in the thermostat. Samples were removed from the bath after given intervals of time and the reaction stopped by chilling the sample in ice water. Nitrogen was then passed through the solution for ten minutes to remove the carbon dioxide, and the solution was titrated with 0.01 *N* sodium hydroxide using brom thymol blue or phenol red as the indicator. In the experiments at the higher percentages of dioxane, sufficient water was added to the sample before analysis that the final composition did not exceed about 30% dioxane. The initial concentrations were so chosen that the first sample removed from the thermostat was approximately 0.01 *N* in trinitrobenzoic acid.

The dioxane was purified by a method similar to that of Hess and Frahm[6] except that the recrystallizations were

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[1] From a dissertation submitted by Dan Trivich to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] Verhoek, THIS JOURNAL, **61**, 186 (1939).

[4] Moelwyn-Hughes and Hinshelwood, *Proc. Roy. Soc.* (London), **A131**, 186 (1931).

[5] Åkerlöf and Short, THIS JOURNAL, **58**, 1241 (1936).

[6] Hess and Frahm, *Ber.*, **71B**, 2629 (1938).

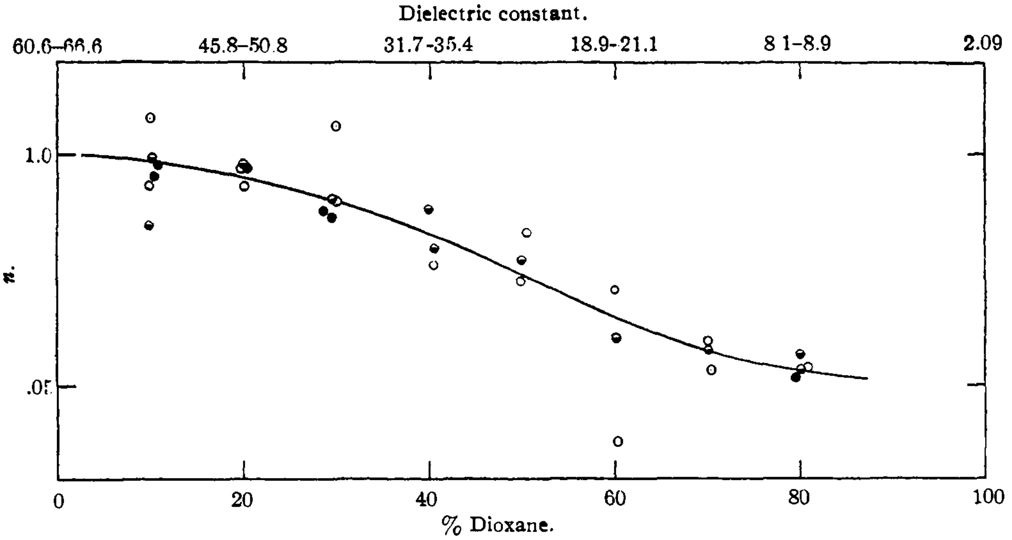

Fig. 1.—The order of reaction for the decomposition of trinitrobenzoic acid in dioxane-water mixtures: ◒, 60°: ○, 70°: ●, 80°.

omitted. The middle third to half of the final distillate was taken as pure product and was stored under nitrogen.

A good commercial grade of 2,4,6-trinitrobenzoic acid was recrystallized twice by dissolving in dry ether and cooling in dry-ice and acetone.

The velocity of the decomposition of trinitrobenzoic acid was determined at approximately 10% intervals for the range of 0–90% dioxane at 60 and 70°, and 0–30% and 80–90% dioxane at 80°. In the range of 40–70% dioxane at 80°, the reaction was too rapid to measure by the procedure described.

The order of reaction was found to change with change in the dioxane content of the solvent. To determine the order, large-scale graphs of concentration of trinitrobenzoic acid against time were made, and the slopes taken at round concentrations. Such values are recorded in the first two columns of Table I for an experiment at 70°, using 59.98% dioxane. A plot of the logarithms of these slopes against log c then gave the order, n, in

$$-\mathrm{d}c/\mathrm{d}t = kc^n \qquad (1)$$

The values of n obtained in this manner are plotted against the percentage of dioxane in Fig. 1. The different symbols represent data for experiments at three temperatures: 60, 70 and 80°. The approximate values of the dielectric constant of the solvent at these temperatures are given at the top of Fig. 1. It may be seen that the value of n is unity in the region of low dioxane content (high dielectric constant) and decreases with increasing dioxane content, but finally levels off to a value of one-half in the region of high dioxane content (low dielectric constant). Further the data do not distinguish any variation of n with temperature.

TABLE I

RATE OF DECOMPOSITION OF TRINITROBENZOIC ACID IN 59.98% DIOXANE AT 70°

Concn., m./l.	$(-\mathrm{d}c/\mathrm{d}t)$, (m./l./sec.) $\times 10^6$	$\dfrac{(-\mathrm{d}c/\mathrm{d}t)}{(\sqrt{1 + 4c/K} - 1)} \times 10^4$
0.008	9.53	3.05
.007	8.96	3.12
.006	7.96	3.05
.005	6.61	2.85
.004	5.55	2.78
.003	4.76	2.88
.002	3.53	2.85
.001	2.27	3.10
		Av. 2.97

In water, 10 and 20% dioxane, where the order is approximately unity, it might be expected that the integrated form of eq. (1) with $n = 1$

$$\ln c = -kt + \text{const.} \qquad (2)$$

could be used. In agreement with this, good straight lines were obtained for plots of log c against time. Similarly for 80 and 90% dioxane with an order of about 0.5, good straight lines were obtained for plots of $\sqrt{c}$ against time in agreement with the integrated form (3), with $n = 0.5$

$$\sqrt{c} = -k't + \text{const.} \qquad (3)$$

Because of the changing order of reaction, it is not possible to compare, on any consistent basis, the values of k, the reaction velocity constants, at the various concentrations of dioxane. Accordingly comparison of the interpolated values of the reaction rate, $(-dc/dt)$, at the arbitrarily chosen concentration of trinitrobenzoic acid 0.008 m./l., is made in Table II. The logarithms of the experimental values at 60, 70 and 80° are plotted against dioxane content in Fig. 2.

TABLE II

VARIATION OF THE RATE OF DECOMPOSITION OF TRINITROBENZOIC ACID WITH CHANGE IN DIOXANE CONTENT OF THE SOLVENT

% Dioxane	$(-dc/dt)_{0.008}$ (m./l./sec.) × 10^6 60°	70°	70.1°	80°
0	1.83	8.93	...	41.5
10	4.59	21.0	21.6	96.6
20	12.9	57.7	58.4	244
30	35.4	152	160	588
40	90.4	346	..	...
50	195	662	597	...
60	274	948	933	...
70	235	668	678	...
80	98.2	276	284	708
89	9.50	24.4	...	71.0
90	6.93	....	...	48.3

As shown by Fig. 2, the reaction rate increases with increasing dioxane content of the solvent in the region of low dioxane content and decreases in the high dioxane region, passing through a maximum at 60% dioxane. The decrease in rate at higher concentrations of dioxane still leaves a faster decomposition rate in 90% dioxane than in pure water, and at the maximum the rate is 150 times as great as in water and 40 times as great as in 90% dioxane.

Activation energies were calculated at 10% intervals of dioxane content. For water and for solutions of approximately 10, 20, 80, and 90% dioxane. where samples of the same solution were used at two different temperatures, activation energies for the ten-degree intervals were obtained using the values of k or k' calculated from the slopes of the plots of $\log c$ against time (equation (2)) and of $\sqrt{c}$ against time (equation (3)). In the intermediate range of dioxane contents the ratio of the reaction rates at 0.008 m./l. for temperatures T_1 and T_2 was substituted for the ratio of velocity constants k_2/k_1

$$\frac{k_2}{k_1} = \frac{[(-dc/dt)_{0.008}]_2}{[(-dc/dt)_{0.008}]_1} \tag{4}$$

This follows from equation (1) since n is independent of temperature within the experimental error.

In Fig. 3, the values for the activation energies obtained by these methods are plotted against percentage of dioxane. The circles represent the 60–70° interval, and the triangles, the 70–80° interval. The solid symbols represent values obtained from the ratio of reaction rates (equation (4)). It may be seen from Fig. 3 that the activation energy decreases steadily with increasing dioxane content, going from a value of 36,000 cal. in water to 22,000 cal. in 90% dioxane.

The Order of Reaction.—According to the mechanism proposed,[3] that the unimolecular decomposition of the trinitrobenzoate ion determines the rate of reaction, one may write

$$-dc/dt = kx \tag{5}$$

where x is the concentration of the trinitrobenzoate ion.

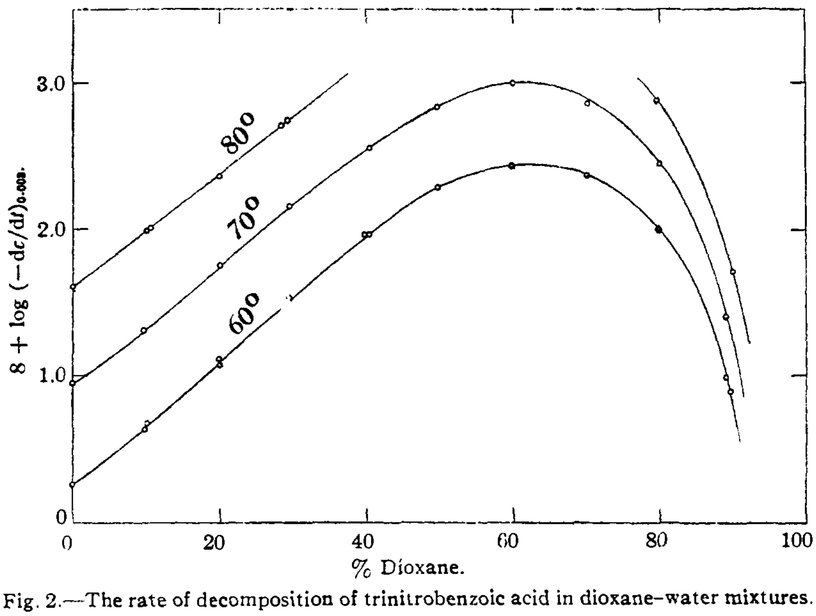

Fig. 2.—The rate of decomposition of trinitrobenzoic acid in dioxane–water mixtures.

Where the acid is completely dissociated, as trinitrobenzoic acid is expected to be in water and solutions of low dioxane content, the concentration of the ion is practically equal to the concentration of the acid, and equation (5) reduces to

$$-dc/dt = kc \tag{6}$$

This is in accord with the experimental data as

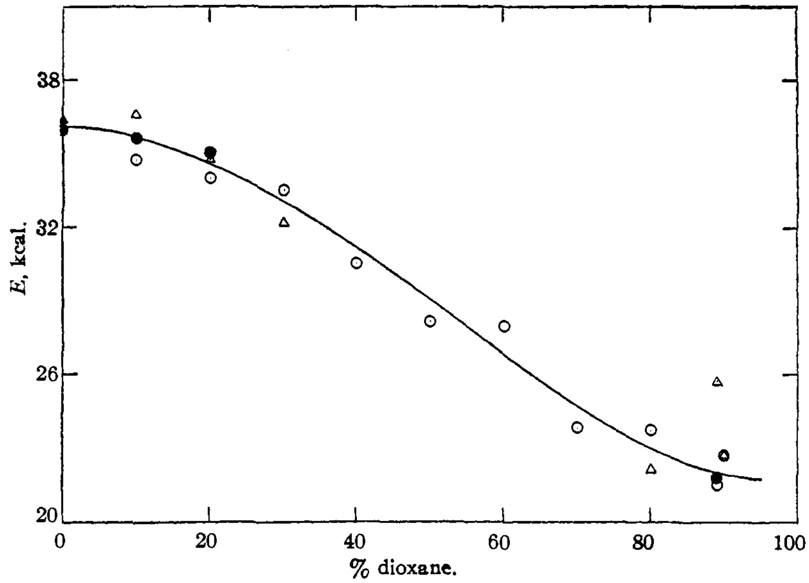

Fig. 3.—Activation energies for the decomposition of trinitrobenzoic acid in dioxane-water mixtures.

shown by Fig. 1 and the fact that good straight lines were obtained for graphs of log c against t.

In any solvent mixture, the concentration of the ion is given by

$$x = -\frac{1}{2}K + \frac{1}{2}\sqrt{K^2 + 4Kc} \qquad (7)$$

$$= \frac{1}{2}K[\sqrt{1 + 4c/K} - 1] \qquad (8)$$

where K is the dissociation constant of the acid in the medium in question.

Therefore, equation (5) becomes

$$-dc/dt = \frac{1}{2}kK[\sqrt{1 + 4c/K} - 1] \qquad (9)$$

When the acid is slightly dissociated (K is very small compared with c), equation (9) reduces to

$$-dc/dt = k\sqrt{Kc} = k'\sqrt{c} \qquad (10)$$

This is expected to be the case in 80 and 90% dioxane where the dielectric constant of the medium is very low. In agreement with these predictions, the order is one-half in 80 and 90% dioxane as shown by Fig. 1, and, further, good straight lines are obtained for graphs of $\sqrt{c}$ against time.

In the intermediate range of dioxane contents, the order of reaction is intermediate between unity and one-half, but a quantitative solution of equation (9) requires a knowledge of the dissociation constant, K. Therefore, the value of K in several mixtures of the solvents was determined.

Dissociation Constants of Trinitrobenzoic Acid in Dioxane-Water Mixtures.—The dissociation constants of trinitrobenzoic acid in 20, 40, 60 and 80% dioxane were determined by a colorimetric method. The work was done at room temperatures, 30–35°, since the acid decomposes at an appreciable rate at higher temperatures. The measurements were made by comparing, at a given wave length, the light transmission of a trinitrobenzoic acid solution containing thymol blue with that of solutions of hydrochloric acid containing the same amount of thymol blue. The concentration of trinitrobenzoic acid was always about 0.008 molar, and the indicator about 10^{-5} molar. The concentration of the hydrochloric acid varied from 10^{-2} to 10^{-4} molar. In 20, 40 and 60% dioxane, the data of Owens and Waters[7] indicate that hydrochloric acid is practically completely dissociated at the concentrations used, so that the concentration of the hydrogen ion was taken to be that of the hydrochloric acid in the solution which graphical interpolation showed to have the same absorption as the trinitrobenzoic acid solution. In 80% dioxane, the hydrogen ion concentration was calculated from the dissociation constant of hydrochloric acid, 3.0×10^{-4} at 35°, interpolated from the data of Owens and Waters.

The dissociation constants obtained are given in Table III.

TABLE III

DISSOCIATION CONSTANTS OF TRINITROBENZOIC ACID IN DIOXANE-WATER MIXTURES

% Dioxane	K
20	3×10^{-1}
40	3.1×10^{-2}
60	2.0×10^{-3}
80	4.7×10^{-6}

The Velocity of Decomposition of the Trinitrobenzoate Ion.—If equation (9) is rearranged to give

$$\frac{-dc/dt}{\sqrt{1 + 4c/K} - 1} = \frac{1}{2}kK \qquad (11)$$

then the left-hand member of equation (11) should be constant over the course of a single experiment.

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[7] Owens and Waters, THIS JOURNAL, 60, 2371 (1938).

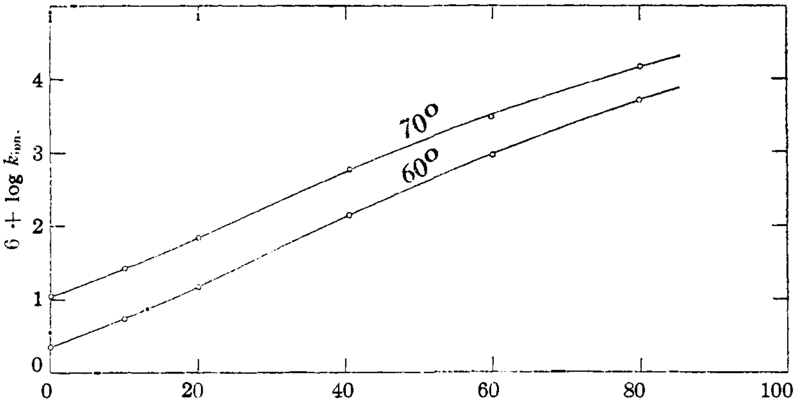

Fig. 4.—The velocity of decomposition of the trinitrobenzoate ion in dioxane–water mixtures.

Calculations of the left-hand side were made for 40, 60 and 80% dioxane at 60 and 70°, using the values of $-dc/dt$ at round concentrations obtained from the large-scale graphs of concentration against time previously mentioned. The third column of Table I shows the results of such a calculation for the experiment at 59.98% dioxane and 70°. For any given experiment, the values calculated in this manner were within 10% of the average value. This is a good verification of equation (11) considering the original accuracy of the dissociation constants and the fact that their values measured at 35° are being applied to experiments at 60 and 70°.[8]

If the values of the constants obtained by equation (11) are multiplied by $2/K$, the values of k, the first-order reaction velocity constant for the trinitrobenzoate ion, are obtained. These values, together with the first-order constants for 0, 10 and 20% dioxane obtained by plotting log c against t, are given in Table IV. In Fig. 4, log k for the ion is plotted against the percentage of dioxane.

TABLE IV

VELOCITY CONSTANTS FOR THE DECOMPOSITION OF THE TRINITROBENZOATE ION IN DIOXANE–WATER MIXTURES

% Dioxane	k_{ion} (sec.$^{-1}$) 60°	70°
0	2.3×10^{-6}	1.1×10^{-5}
10	5.5×10^{-6}	2.7×10^{-5}
20	1.5×10^{-5}	7.0×10^{-5}
40	1.4×10^{-4}	5.8×10^{-4}
60	9.2×10^{-4}	3.0×10^{-3}
80	5.2×10^{-3}	1.5×10^{-2}

Figure 4, in contrast to Fig. 2, shows that the reaction velocity of the trinitrobenzoate ion does not pass through a maximum, but increases steadily with increasing dioxane content.

Regarding k as the fraction of the ions decomposing per unit time, it may be seen that the reaction rate, $(-dc/dt)$, is given by the product of k and the concentration of the ion. In the region of low dioxane content, as the percentage of dioxane is increased, the concentration of the ion is decreased but slightly while k, the fraction of ions decomposing, is increased so much that the actual number of ions decomposing is increased. This increase in reaction rate continues up to 60% dioxane, after which the concentration of the ion decreases with increasing dioxane content so that, in spite of the fact that a greater fraction decomposes, the number of ions decomposing decreases. Thus the ionic mechanism is successful in explaining the maximum in the reaction rate.

Solvent Effects.—The increase in the reaction velocity constants of the ion with increasing dioxane content is reflected in the lowered activation energy as shown in Fig. 3. This decrease in activation energy with increasing dioxane content is presumed, in accordance with a suggestion previously made,[3,9] to be due to the changing character of the solvation of the ion. In water, hydration serves to stabilize the trinitrobenzoate ion so that a greater amount of energy is required to decompose the hydrated ion than would be required if it were not hydrated. As the dioxane content of the solvent is decreased, the degree of hydration of the ions is decreased, resulting in the decreased activation energy and the corresponding increase in reaction rate.

If the values of k for the trinitrobenzoate ion are used in the equation

$$k = se^{-E/RT} \qquad (12)$$

to calculate values for s, it is found, as is frequently the case, that s decreases as E decreases. As E

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(8) The measurements of acid dissociation constants in dioxane–water mixtures by Harned and co-workers (THIS JOURNAL, **63**, 2579, 3308 (1941); **65**, 54 (1943)) in the temperature interval 0–50° indicate that the dissociation constants at the higher temperature will not be greatly different from those at 35°. Further, Harned's work shows that the temperature coefficient of the dissociation constants is not markedly different in solvent mixtures containing different dioxane–water ratios, a factor which becomes important in comparing activation energies for the trinitrobenzoate decomposition at different dioxane–water ratios, *vide infra*.

(9) Verhoek, *ibid.*, **56**, 571 (1934).

changes from 36,000 calories in water to 23,000 calories in 80% dioxane, the value of ln *s* changes from 41.2 to 30.3.

It is interesting to note here the relative magnitudes of the effects of solvation and of the dielectric constant on this reaction. If solvation were a relatively unimportant factor, then, as the dielectric constant of the solvent decreases with increasing dioxane content, the concentration of the trinitrobenzoate ion decreases for any given acid concentration, and the reaction rate should decrease. However, as shown by Table I and Fig. 2, the reaction rate increases markedly with increasing dioxane content up to 60% dioxane. It is thus evident that the changing solvation of the ion is an important factor in determining the rate of reaction. Further it indicates that caution must be used in interpreting the data obtained in studies of reactions involving ions when the composition of the medium is changed in order to effect a change in the dielectric constant. In some cases, this may result in attributing solely to changes in the dielectric constant effects which are due in part to changes in the extent of solvation of the ions involved.

Summary

1. The order of reaction of the decarboxylation of 2,4,6-trinitrobenzoic acid in solvent mixtures of dioxane and water has been found to change in a continuous manner from a value of unity in solutions of low dioxane content to one-half in solutions of high dioxane content.

2. The reaction rate increases with increasing dioxane content of the solvent in the region of low dioxane content and decreases with increasing dioxane content in the region of high dioxane content, passing through a maximum at 60% dioxane.

3. The activation energy decreases continuously with increasing dioxane content from a value of 36,000 cal. in water to 22,000 cal. in 90% dioxane.

4. The variation in the order of the reaction and the maximum in the reaction rate have been explained as being due to the decomposition of the trinitrobenzoate ion. Measurements of the dissociation constants of trinitrobenzoic acid in several solvent mixtures of dioxane and water were made and used to verify this explanation quantitatively.

5. The variation of the activation energy has been related to varying degrees of solvation of the trinitrobenzoate ion.

COLUMBUS, OHIO RECEIVED MAY 6, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Boron. I. Preparation and Properties of Pure Crystalline Boron

BY A. W. LAUBENGAYER, D. T. HURD,[1] A. E. NEWKIRK[1] AND J. L. HOARD

Progress in the preparation and determination of the properties of boron has been reviewed in a recent paper[2] and the surprising dearth of exact information about the element has been shown to be due to the considerable difficulties encountered in attempts to prepare pure boron, especially in the massive single crystalline form. Great confusion exists because of the general practice of using the term "crystalline boron" for the crystals which have been shown[3] to be AlB_{12}, obtained when powdered boron is added to molten aluminum.[4] Winslow and Liebhafsky[5] have recently reported very low purity for various commercial supplies of "pure boron" which they analyzed.

In the present investigation we have undertaken the production of single crystals of boron, the establishment of the high purity of the samples, a comprehensive study of the properties of the element and, in particular, X-ray examination of the material in an effort to ascertain the X-ray powder diffraction pattern characteristic of boron and to obtain data adequate for the determination of its crystal structure.

Preparation of Boron

On the basis of a critical study of the methods which have been used for obtaining elementary boron, the procedure involving the deposition of the element on a hot filament was selected as offering the most promise. The general experimental technique, which we shall refer to

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(2) Laubengayer, Newkirk and Brandauer, *J. Chem. Ed.*, **19**, 382 (1942).

(3) Wöhler, *Ann.*, **141**, 268 (1867); Hampe, *ibid.*, **183**, 75 (1876).

(4) Wöhler and Deville, *Compt. rend.*, **46**, 888 (1857); *Ann.*, **101**, 118 (1857) and **105**, 67 (1858); *Ann. chim. phys.*, [3] **52**, 63 (1858).

(5) Winslow and Liebhafsky, THIS JOURNAL, **64**, 2725 (1942).