

ying in acid solution a single step reduction with *p*-nitrophenol at the dropping mercury electrode, but a two-step reduction with *o*-nitrophenol because of the formation of a more stable intermediate. We have not observed any large differences between the two phenols, but instead find about the same fraction of stannic tin present in both cases.

Acknowledgment.—One of us (C.V.) wishes to express his gratitude for a du Pont Fellowship during the year 1948–1949.

Summary

1. The kinetics of the reduction of aromatic nitro compounds by tin and hydrochloric acid has been studied under various conditions of acidity, temperature and stirring, the oxygen being removed from the system with carbon dioxide.

2. In the proposed mechanism, the nitro compound diffuses to the surface where it is rapidly reduced to an intermediate, a fraction of which escapes further reduction at the surface

by diffusing back into solution where its subsequent reduction results in formation of stannic compounds.

3. The rate law based on the mechanism agrees with the experimental data for both stannous and total tin concentration over the entire course of the reaction.

4. The variation of the rate constants is completely in accord with the diffusion theory of heterogeneous reactions.

5. The existence of a transitory intermediate reduction product is indicated by the formation of stannic compounds in amounts much larger than would be produced by the homogeneous reaction between stannous chloride and the nitro groups, and is supported by the results of varying the stirring rate.

6. The formation of an intermediate reduction product during the reaction indicates that the reduction of the nitro groups proceeds not by a single step but by two or more successive steps under these experimental conditions.

IOWA CITY, IOWA

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO AND THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Acid-Base Studies in Gaseous Systems. VI. A Simplified Technique for Dissociation Measurements

BY HERBERT C. BROWN¹ AND MELVIN GERSTEIN²

In the first paper of this series³ there was described a technique for making precise measurements of the dissociation of addition compounds. Since that time a simplified technique has been developed for the determination of the thermodynamic constants for the dissociation reaction. Moreover, the dissociation tensimeters used in these investigations have undergone a number of improvements in design. It is the purpose of the present paper to describe these developments.

The Dissociation Tensimeter

The most recent design of the dissociation tensimeter is shown in Fig. 1. For details of operation see the first paper of this series.³

The tensimeters have been increased in size over the original models to 400–500 ml. in order to minimize the effects of surface adsorption and errors involved in bringing the mercury in the manometer, M, back to the zero point, Z.

The simple mercury seal in the original design has been replaced by a ground joint sealed by mercury, S. In practice 100–200 mm. of dry air is placed above the mercury seal. Vaporization of the mercury at elevated temperatures is minimized and a source of possible error from tempera-

ture inhomogeneity at the mercury seal is thereby eliminated. The enclosed iron rod, J, manipulated with the aid of a magnet, maintains the seal open while samples are introduced or removed.

Changes in the construction of the ground-joint, G, increase somewhat the constructional difficulties over those involved in the original design. However, the new design is more rugged than the old, reduces the quantity of mercury required in the mercury reservoir, MR, and minimizes the danger of air entering the apparatus through the ground joint, G, when the mercury level in the reservoir is low.

A more rigid, sturdier construction has been achieved by the introduction of the two bridges, B.

The Method of Matched Samples

In the method of matched samples, the volumes of two dissociation tensimeters are matched to within 1 part in 2000. The two components are individually measured out, one in each tensimeter, at a temperature and pressure (usually about 20.00 mm.) such that van der Waals deviations are negligible. The sizes of the two samples are adjusted until the pressures are equal to within 1 part in 2000. With the aid of liquid nitrogen the more volatile of the two components (usually trimethylboron) is quantitatively transferred into

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(3) Brown, Taylor and Gerstein, *THIS JOURNAL*, **66**, 431 (1944).

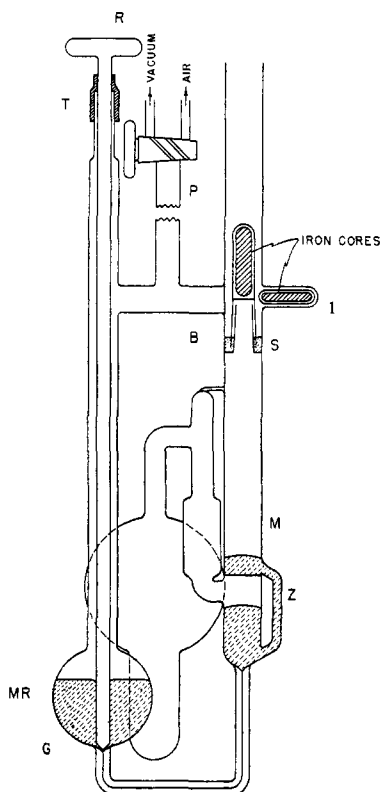


Fig. 1.—Dissociation tensimeter.

the tensimeter holding the second component. The two components react to form the addition compound. The temperature is now raised until the material is completely volatilized and measurements of the pressures exerted by the gaseous product are made at a number of temperatures.

The data permit calculation of α , the degree of dissociation, K_p , the equilibrium constant, and ΔH , the heat of dissociation. The method is capable of determining K_p and ΔH with a high degree of precision.³ However, there are certain disadvantages. (1) The two samples must be matched to within 1 part in 2000. Thus, samples of 20.00 mm. must be matched to within 0.01 mm. This operation is quite tedious. (2) The lowest pressure that can be accurately measured on the manometer is in the neighborhood of 20.00 mm. The minimum pressure exerted by a highly dissociated addition compound, synthesized from two samples of this magnitude, will be in the neighborhood of 40.00 mm. However, to avoid deviations from the perfect gas laws, it would often be desirable to measure the dissociation pressures in a lower pressure range, particularly in the case of addition compounds of relatively low volatility. (3) Impurities of the order of 0.1% in either of the two components may be detected and can seriously affect the accuracy of the data.

These difficulties led us to develop a simpler procedure which does not require careful matching of the two components, which permits operation

at lower pressures, and which tolerates larger quantities of impurities in the two components. This method has been termed the "method of approximations."

The Method of Approximations

The method of approximations is based upon the assumption that over the relatively short temperature range that the dissociation is usually studied, 40–50°, the heat of dissociation ΔH may be considered to be constant. Therefore, only the correct value of the size of the sample yields a linear relationship between $\log K_p$ and $1/T$ as required by the equation

$$\frac{d \ln K_p}{d 1/T} = \frac{-\Delta H}{R}$$

In this procedure the two components are purified, using only relatively simple precautions. A sample of the addition compound is synthesized, purified by distillation in the high vacuum apparatus, and introduced into the tensimeter. The temperature is raised until the sample is completely vaporized, and a series of 8 to 10 pressure measurements is then made, usually at 5° intervals.

A value for the size of the sample is chosen arbitrarily and used to calculate the equilibrium constants for five different temperatures, approximately evenly spaced over the temperature range studied. If the size selected for the sample is too low, a curve drawn through the calculated equilibrium constants in the usual $\log K$ vs. $1/T$ graph will be concave upward. If the size selected is too high, the curve will be concave downward. The value for the sample size is then varied until the calculated equilibrium constants yield a straight line.

The number of approximations which are made can be greatly reduced by proceeding systematically to the correct solution. Thus, the first approximation is usually made by assuming that the addition compound is completely dissociated at the highest temperature studied. A second approximation is then made by drawing a straight line through the lower points and calculating the size of the sample from the extrapolated value of the equilibrium constant at the higher temperatures. This procedure is repeated until the data satisfactorily define a straight line. The effect of changes as small as 0.01 mm. in the size of the sample produce a noticeable effect on the curvature of the line.

A small fraction of the addition compound (10–20%) may now be distilled away and the determination repeated. If the addition compound is of satisfactory homogeneity, the results of the two determinations will be in good agreement.

A typical determination of trimethylamine-trimethylboron is repeated in Tables I and II. The successive approximations and final results are illustrated in Fig. 2.

TABLE I

REPRESENTATIVE DATA FOR THE DISSOCIATION OF TRIMETHYLAMINE-TRIMETHYLBORON
(Preliminary Approximations)

Temp., °C.	70.0	81.2	90.8	102.0	112.9
$P_{\text{obs.}}$, mm.	50.74	55.99	59.78	63.35	66.17
First approximation: $P_0 = 23.54^a$					
$P_{\text{calcd.}}$, mm.	29.57	30.54	31.37	32.33	33.27
Deg. of dissoci.,	0.7159	0.8333	0.9056	0.9595	0.9889
K (atm.)	0.0702	0.167	0.359	0.966	3.85
Second approximation: $P_0 = 23.78^b$					
$P_{\text{calcd.}}$, mm.	29.87	30.85	31.69	32.66	33.61
Deg. of dissoci.,	0.6987	0.8149	0.8828	0.9355	0.9647
K (atm.)	0.0637	0.150	0.288	0.629	1.33
Third approximation: $P_0 = 23.83^b$					
$P_{\text{calcd.}}$, mm.	29.94	30.91	31.75	32.75	33.68
Deg. of dissoci.,	0.6947	0.8114	0.8828	0.9355	0.9647
K (atm.)	0.0623	0.142	0.278	0.584	1.17

Final approximation: $P_0 = 23.85^b$

^a Obtained by assuming addition compound at 118.8° ($P_{\text{obs.}} = 67.55$) to be 100% dissociated. ^b Obtained by extrapolation to 118.8° point.

TABLE II

DISSOCIATION DATA FOR TRIMETHYLAMINE-TRIMETHYLBORON
(Method of Approximations)

Temp., °C.	Pressures, mm.		Degree of dissociation α	Dissociation constant K (atm.)
	Observed	Calculated ^a		
70.0 ^b	50.74	29.96	0.6936	0.0619
76.0	53.66	30.49	.7599	.0965
81.2 ^b	55.99	30.94	.8096	.140
85.2	57.66	31.29	.8428	.186
90.8 ^b	59.78	31.78	.8811	.273
96.5	61.74	32.28	.9126	.405
102.0 ^b	63.35	32.76	.9338	.568
107.3	64.80	33.22	.9506	.799
112.9 ^b	66.17	33.71	.9629	1.11
118.8	67.55	34.22	.9740	1.64

^a Calculated using final approximation, $P_0 = 23.85$.

^b Points used for approximations.

Discussion

The thermodynamic data for the dissociation of trimethylamine-trimethylboron by the method of approximations are summarized in Table III together with previously reported data for this compound obtained by the method of matched samples.³

TABLE III

SUMMARY OF DISSOCIATION DATA FOR TRIMETHYLAMINE-TRIMETHYLBORON

Method	K_{100}	ΔF_{100}°	ΔH	ΔS
Matched samples	0.472	557	17,620	45.7
Approximations	.501	512	17,660	45.9

The agreement in the results obtained by the two different procedures may be considered satisfactory in view of the probable lower accuracy of the method of approximations resulting from the simplifications introduced.

Further confirmation of the method is furnished by results obtained with the addition compounds

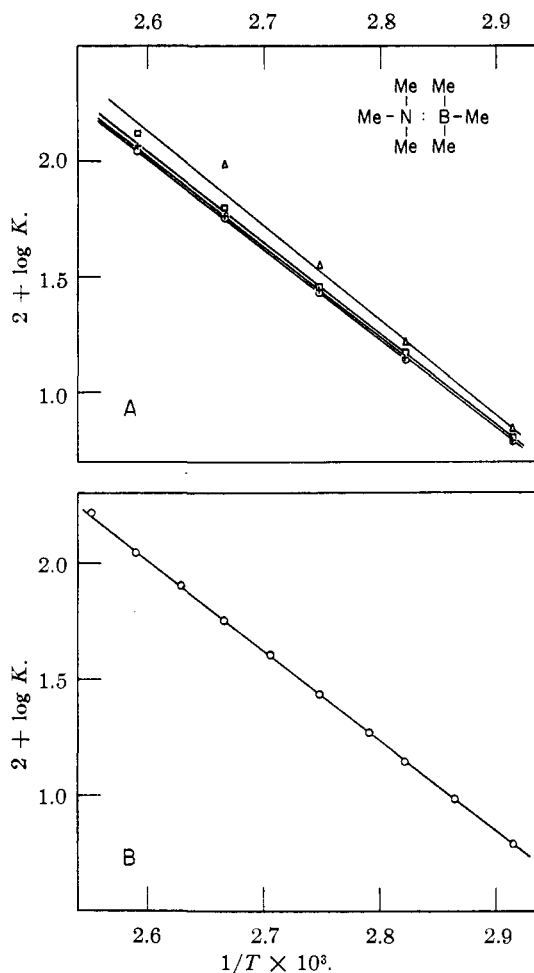


Fig. 2.—Trimethylamine-trimethylboron: A, approximations; B, final dissociation line.

of trimethylboron and the cyclic imines,⁴ most of which were studied by both procedures.

The method of approximations overcomes the main disadvantages of the method of matched samples. It requires but one tensimeter, rather than a matched pair of tensimeters. The size of the tensimeter need not be known. The components do not need to be carefully matched. The size of the sample of the addition compound can be relatively small, such that the pressures exerted by the vaporized sample are approximately 20 mm. By using such small samples and working in the low pressure region the effects of van der Waals deviations can be minimized. Finally, it is a relatively simple matter to remove from the two components all impurities which differ markedly in volatility from each of the components. The two components react to form an addition compound of much lower volatility. Such volatile impurities as might have remained in the components before reaction, can now be separated from the less volatile product. More-

(4) Brown and Gerstein, *THIS JOURNAL*, **72**, 2926 (1950).

over, the homogeneity of the product may be established by carrying out separate determinations on individual fractions.

Two possible objections to the method of approximations exist. The individual approximations require tedious calculations. These might be reduced by the development of mathematical, rather than graphical, procedures for handling the data. Such a method was developed but in practice offered no advantage over the graphical procedure here described.⁵ Again, a marked curvature in the $\log K$ versus $1/T$ plot might occur and lead to serious errors in the calculated results. However, up to the present time, such curvatures in the dissociation of addition compounds have been rarely encountered, and can then be avoided by working at lower pressures.

(5) This mathematical procedure is described in the Ph.D. Dissertation by Melvin Gerstein, "Acid-Base Studies in Gaseous Systems: The Dissociation of the Addition Compounds of Trimethylboron with Cyclic Imines," The University of Chicago Libraries, Chicago, Ill., September, 1945.

In view of the many advantages of, and the minor objections to, the method of approximations, this method appears highly promising for the determination of dissociation data for addition compounds.

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Summary

1. An improved dissociation tensimeter is described.

2. A simplified method has been developed for determining the dissociation constants of addition compounds from tensiometric data by means of a graphical method of approximations.

3. The procedure has been applied to trimethylamine-trimethylboron. The results are in good agreement with earlier data obtained by the method of matched samples.

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Acid-Base Studies in Gaseous Systems. VII. Dissociation of the Addition Compounds of Trimethylboron and Cyclic Imines; I-Strain

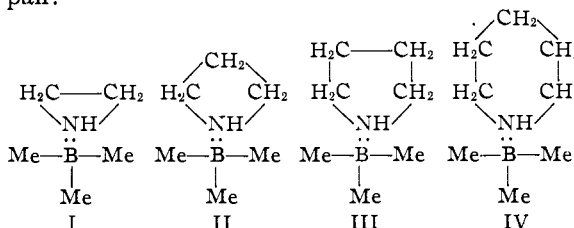
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Years ago Baeyer³ pointed out that five- or six-membered rings were relatively easily formed and stable, whereas three- and four-membered rings appeared to be less readily formed and to be less stable. He attributed these differences between the three- and four-membered rings on the one hand and the five- and six-membered rings on the other to the strain involved in deforming the bond angle from its usual tetrahedral value ($109^{\circ}28'$) to the 60 and 90° values required by the geometry of the small rings. With the years Baeyer's views on the effect of strain on the stability of three- and four-membered ring systems have received much experimental verification.⁴

Although there is now considerable evidence as to the effect of ring strain on the stability of small-membered rings, there is as yet relatively little information available on the effect of such ring strain on chemical properties which do not involve ring opening. For example, it would be of interest to know how ring strain affects the

base strengths of ethylenimine and trimethylenimine. Unfortunately, these strained rings undergo rather rapid ring opening in aqueous solution⁵ and measurement of the ionization constants of the bases offers experimental difficulties. Moreover, such data in aqueous solution would involve the usual difficulties in interpretation.

Experiment revealed that the addition compounds of trimethylboron with these cyclic imines were stable substances and did not undergo chemical change under the conditions required for measurement of the dissociation constants. Accordingly, it was decided to prepare and study the addition compounds of trimethylboron with ethylenimine (I), trimethylenimine (II), pyrrolidine (III) and piperidine (IV), in order to examine the effect of ring strain on the ability of the nitrogen atom to donate its electron pair.



(5) Freundlich and Neumann, *Z. physik. Chem.*, **57**, 69 (1914).

(1) Department of Chemistry, Purdue University, Lafayette, Ind.

(2) National Advisory Committee for Aeronautics, Cleveland, Ohio.

(3) Baeyer, *Ber.*, **18**, 2269 (1885).

(4) W. Hückel, "Der Gegenwärtige Stand der Spannungstheorie," *Fortschritte der Chemie, Physik und Physikalischen Chem.*, Serie A, Band 19, Heft 4, edited by A. Eucken, Gebrüder Bornträger, Berlin, 1927.