(3) **The angle θ for position 3 is almost 90°.** Reason: a methyl group in this position produces little change in intensity.

The effect of substituents in the 2-positions, which probably produce steric hindrance, may be treated by the same perturbation theory, as long as the changes in intensity are relatively small. However, the perturbation vectors in this case are no longer necessarily coplanar with the perturbation vectors produced by substituents at other positions.

These general theoretical conclusions support and validate Beale and Roe's important experimental demonstration that *in a strong transition the intensity increments from substituents in particular positions are additive.*

Independent determination of m_a and θ_a at particular positions does not seem feasible for strong transitions (though it can be done for forbidden transitions[6]). If we assume m_a constant for a given substituent at all positions, θ_a can be approximately determined from the intensity increments except for an ambiguity of sign.

I am indebted to Drs. Beale and Roe for showing me their manuscript in advance of publication.

(6) J. R. Platt, "Electronic Structure and Excitation of Polyenes and Porphyrins," Chapter 4, Vol. 3 of "Radiation Biology," Ed., S. Hendricks, McGraw-Hill Book Co., Inc., New York, N. Y., 1952.

PHYSICS DEPARTMENT
UNIVERSITY OF CHICAGO
CHICAGO, ILL.

RECEIVED NOVEMBER 1, 1951

Autocatalyzed Hydrolysis of Sucrose by Acid

BY LAWRENCE J. HEIDT, F. WILLIAM SOUTHAM AND EDWARD A. SULLIVAN[1]

RECEIVED FEBRUARY 4, 1952

The rate of hydrolysis of sucrose by acid has been the subject of numerous investigations for over a century. Under the usual conditions in a given experiment at constant temperature, the effective concentration of the acid remains unchanged and the reaction is first order with respect to the concentration of the sucrose. We have found the reaction to be autocatalyzed as much as six-fold by a corresponding increase in the acidity under conditions where the increase in acidity on a mole basis corresponds to less than one-tenth per cent. of the sucrose hydrolyzed.

The reactions were carried out in sealed, clean, acid- and alkali-free, Kimble flasks placed in a bath whose temperature was controlled and recorded continuously to ±0.03°. Reaction was stopped by bringing the *p*H to 6 ± 0.2 by adding a solution of sodium bicarbonate to the reaction mixture in the bath. Loss of water from the reacting mixture or neutralized solution amounted to less than 1% in all cases.

The fraction of the sucrose hydrolyzed was determined in a manner previously described[2] from measurements of the reducing power of the solution toward a carbonate buffered cupritartrate reagent[3] at *p*H 8.7. The method eliminates any correction for mutarotation of the liberated sugars. The

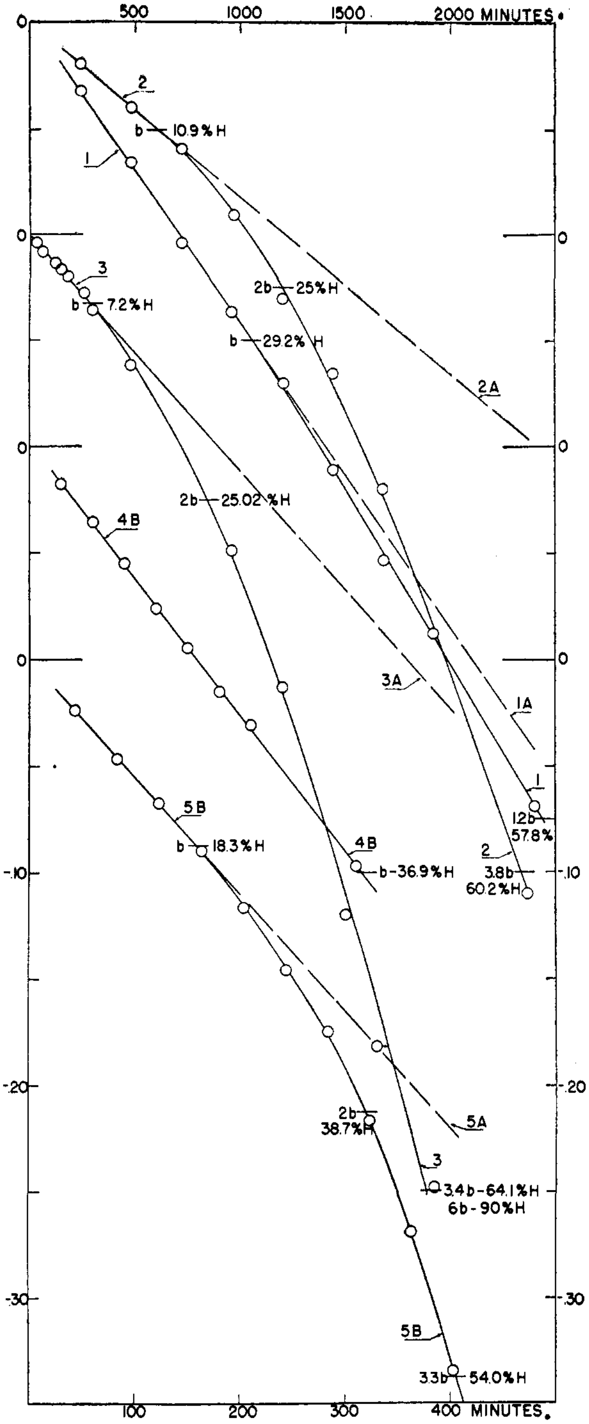

Fig. 1.—Evidence for autocatalysis in the hydrolysis of sucrose by acid. Common logarithms of one minus the fractional hydrolysis of sucrose are plotted as ordinates against the lengths of time the reaction has taken place under the conditions tabulated below. The curves would be straight lines if there were no measurable autocatalysis as is the case for curve 4B. The usual first-order rate constant equals $-2.303b$. The concentrations given below are the initial formal values at 0° in moles of acid per liter of solution and in g. sucrose (within 1 mg.) in the volume given in ml. (within 0.1 ml.). No color developed in any of the solutions. The % H in the fig. gives the % sucrose hydrolyzed.

Curve	Temp. °C.	10^4(HCl)	Sucrose	Time scale
1	75.10	1.05	2g./100 ml.	Upper
2	75.10	1.05	13g./55 ml.	Upper
3	75.10	2.7	80g./100 ml.	Upper
4B	75.10	5.4	80g./100 ml.	Lower
5B	95.10	1.05	13g./55 ml.	Lower

---

[1] The authors are indebted to the Sugar Research Foundation, Inc., for a grant-in-aid.

[2] L. J. Heidt and C. B. Purves, THIS JOURNAL, **66**, 1385 (1944).

maximum reducing power was determined in critical cases, such as represented by curve 3, Fig. 1, and was found to be within 3% of the value calculated for the conversion of all the sucrose into invert sugar.

The sucrose was a finely ground dry sample of Domino cane sugar, adant cut loaf, over 99.9 wt. % sucrose containing less than 0.018 wt. % invert sugar.[3] The water was triply distilled and was free of all impurities. The other materials were of analytical reagent or C.P. quality.[2]

The results are presented in Fig. 1. In the case of curve 3 autocatalysis increased the rate of the reaction sixfold (6b) by the time 90% of the sucrose had been hydrolyzed, and this was accompanied by a decrease in the *p*H of the reacting mixture. The increase in the acidity corresponded quantitatively to the increase in the rate. The *p*H values were measured with a glass electrode after the solutions had been cooled to 25°.

The extent of the autocatalysis was found to increase when there was an increase in (1) the per cent. sucrose hydrolyzed (curve 3), (2) the initial concentration of sucrose (*cf.* curves 1 and 2), (3) the temperature at which the hydrolysis was carried out (*cf.* curves 2 and 5B) and when there was (4) a decrease in the initial concentration of the acid (*cf.* curves 3 and 4B).

(3) L. J. Heidt and F. W. Southam, THIS JOURNAL, **72**, 580 (1950).

Boron-Nitrogen Systems. II. Diethylaminoboron Dichloride[1]

BY ROBERT C. OSTHOFF[2] AND CHARLES A. BROWN

RECEIVED JANUARY 5, 1952

The first paper of this series[3] was devoted to a discussion of the physical and chemical properties of dimethylaminoboron dichloride, in both its monomeric and dimeric forms. In this paper the properties of diethylaminoboron dichloride, $(CH_3CH_2)_2NBCl_2$, will be discussed.

Wiberg[4] has reported the preparation of diethylaminoboron dichloride by the action of boron trichloride upon diethylamine, but no yield data or experimental details were presented. Wiberg also found that diethylaminoboron dichloride formed no dimer, even after standing for one year at room temperature. This lack of dimer formation is in sharp contrast to the behavior of dimethylaminoboron dichloride which readily forms a rather stable dimer.[3] It was stated by Wiberg that diethylaminoboron dichloride reacts with hydrohalogen acids and with tertiary amines, but the properties of the resulting compounds have not been published.

Experimental

Preparation of $(CH_3CH_2)_2NBCl_2$.—Diethylaminoboron dichloride was obtained by fractionation of the reaction mixture which resulted from the action of excess boron trichloride (Matheson) upon diethylamine (Eastman Kodak Co. "White Label") used as supplied by the manufacturer without further purification, since none of the contaminants would give rise to products which would decrease the purity of the diethylaminoboron dichloride. The reactants were brought together at −196° *in vacuo*. By warming the reaction mixture slowly to room temperature (over about a 4-hour period) it was possible to fractionate the volatile products by passing them through traps at −20, −80 and −196°. Diethylaminoboron dichloride was collected in the trap which was held at −20° and further purified by bulb to bulb vacuum distillation. Based on the amount of diethylamine that was employed, the yield of product was 40%; the calculation of the yield was made by assuming that the preparative reaction may be formulated as

$$BCl_3 + 2HN(CH_2CH_3)_2 \longrightarrow (CH_3CH_2)_2NBCl_2 + (CH_3CH_2)_2NH{\cdot}HCl$$

A mole ratio of amine to boron trichloride of about 1.5 was used in the preparation of diethylaminoboron dichloride in order that none of the higher substitution products of boron trichloride (*i.e.*, bisdiethylaminoboron chloride and trisdiethylaminoboron) would be formed.

Characterization of Diethylaminoboron Dichloride.—In Table I are summarized the physical properties of diethylaminoboron dichloride which have been reported previously by Wiberg,[4] as well as the corresponding values which were observed by the authors.

The authors determined the melting point visually; the boiling point, the heat of vaporization, and the Trouton constant were evaluated by the authors from a study of the vapor pressure of the pure compound as will be described below. The experimental methods employed by Wiberg for the evaluation of these constants are not given in the literature.

TABLE I

PHYSICAL PROPERTIES OF DIETHYLAMINOBORON DICHLORIDE

Property	Reported by Wiberg[4]	Observed
M.p., °C.	−25.5	−23.0
B.p., °C.	150	148
Heat of vaporization, cal./mole	9560	9480
Trouton constant, cal./deg.	22.6	22.5

Measurements of vapor density at 22° by the authors gave an observed molecular weight of 151 (calcd. for $(CH_3CH_2)_2NBCl_2$, 153.9). It had been reported earlier by Wiberg[4] that this compound remained monomeric after standing at room temperature for one year. This was observed to be the case, since the authors found no evidence of dimer formation in samples which were stored for 18 months at room temperature in the absence of air and moisture. When sealed tubes of diethylaminoboron dichloride were heated to 190° in attempts to form a dimer, we observed only carbonization of the ethyl groups.

Liquid Density.—A dilatometric pycnometer was employed to evaluate the density of liquid diethylaminoboron dichloride in the temperature range of 5 to 95°. By application of the method of least squares to the observed data, the linear equation relating the density to the Centigrade temperature was found to be

$$d = 1.0796 - 0.001161\,t\ (\text{g./ml.})$$

Some of the observed and calculated values of the density are summarized in Table II. These values of the density were estimated to be accurate to about 0.05%.

Vapor Pressure.—By employment of isoteniscopes of the type described by Smith and Menzies,[5] the vapor pressure of diethylaminoboron dichloride was studied between 24 and 140°. In order to ensure the removal of adsorbed water from the isoteniscopes, the apparatus was repeatedly flamed in high vacuum. Above 80° each of the observed pressures was corrected by the subtraction of the vapor pressure of mercury at that temperature.

By application of the method of selected points to the vapor pressure data of two independent runs, the constants of the Antoine[6] equation were evaluated. Thus the vapor

---

[1] Taken from Ph.D. thesis of Robert C. Osthoff, Harvard University, 1951.

[2] Procter and Gamble Fellow in Chemistry, Harvard University, 1951. Present address: Research Laboratory, General Electric Co., Schenectady, N. Y.

[3] C. A. Brown and R. C. Osthoff, THIS JOURNAL, **74**, 2340 (1952).

[4] E. Wiberg, "Fiat Review of German Science," Vol. 23, Part I, pp. 217, *et seq.*

[5] A. Smith and A. W. C. Menzies, THIS JOURNAL, **32**, 1412 (1910).

[6] G. W. Thomson, *Chem. Revs.*, **38**, 1 (1946).