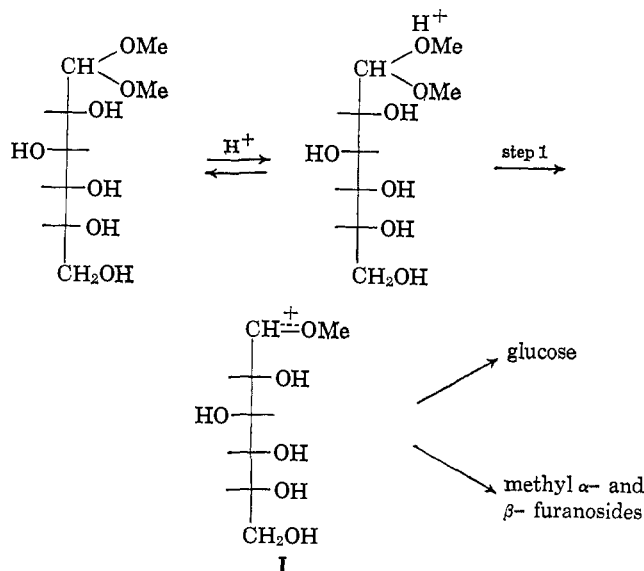
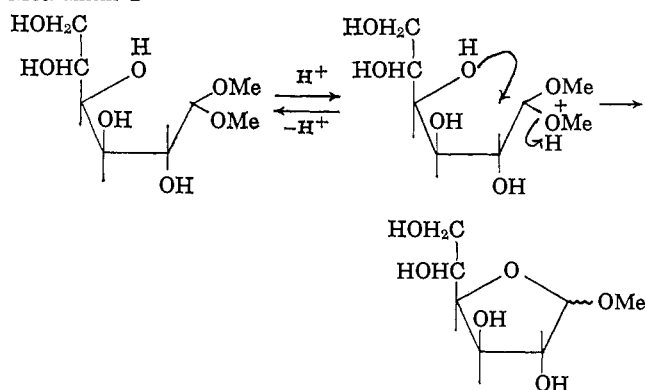


Mechanism 1



Mechanism 2



ring closure of the glucose acetal is 340 times and the galactose acetal 29 times greater than the estimated unassisted rate of ionization of a pentahydroxyhexanal acetal based on the  $\rho^*\sigma^*$  relationship. The rates of ring closure are also substantially greater than the ob-

Table II. Second-Order Rate Constants for the Acid-Catalyzed Hydrolysis and Ring Closure of Some Dimethyl Acetals at 25°

Reaction	10 <sup>4</sup> .		
	10 <sup>4</sup> k l. mole <sup>-1</sup> sec. <sup>-1</sup>	k <sub>calcd</sub> <sup>a</sup> sec. <sup>-1</sup>	k/k <sub>calcd</sub>
Hydrolysis of D-glyceraldehyde acetal	1.77	2.48	.71
Ring closure of D-glucose acetal	110	.324	340
Ring closure of D-galactose acetal	9.3	.324	29

<sup>a</sup> Calculated rate of ionization using Taft's  $\rho^*\sigma^*$  equation based on a value for the second-order rate constant for the hydrolysis of acetaldehyde dimethyl acetal of  $2.74 \times 10^{-1}$  l. mole<sup>-1</sup> sec.<sup>-1</sup> (Tables of Chemical Kinetics, National Bureau of Standards Circular 510, 1951, p. 22).  $\rho^*$  was assumed to be -3.65 and  $\sigma^*$  for the first hydroxymethyl group to be 0.555 (M. M. Kreevoy and R. W. Taft, *J. Am. Chem. Soc.*, **77**, 5590 (1955)).  $\sigma^*$  values for the other hydroxyl groups were calculated from this, assuming an attenuation factor of 0.5 for each additional carbon atom between the hydroxyl group and the reaction center (J. C. McGowan, *J. Appl. Chem.*, **10**, 312 (1960)).

served rate of hydrolysis of D-glyceraldehyde dimethyl acetal. Since hydroxyl substituents cause a decrease in the rate of hydrolysis of acetals through their inductive effect, the rate constant of this latter reaction sets an upper limit on the unassisted rate of ionization for the

glucose and galactose acetals. It is therefore concluded that the ring closure of the glucose and galactose acetals involves a nucleophilic attack synchronous with the rupture of the acetal bond.

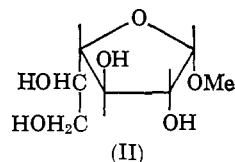
Nucleophilic attack synchronous with the acid-catalyzed rupture of a glycosidic bond possibly occurs also in the hydrolysis of aldofuranosides. In Table III

Table III. Entropies of Activation (cal. deg.<sup>-1</sup> mole<sup>-1</sup>) for the Hydrolysis of Some Glycosides

	Furanosides, 1 M HClO <sub>4</sub> at 25°	Pyranosides, <sup>a</sup> 1 M HCl at 60°
Methyl $\alpha$ -D-gluco-	-11.1	+14.8
Methyl $\beta$ -D-gluco-	-9.0 <sup>b</sup>	+16.5
Methyl $\alpha$ -D-galacto-	-9.4	+17.7
Methyl $\beta$ -D-galacto-	-8.7	-13.3
Methyl $\alpha$ -D-xylo-	-8.3	+15.7
Methyl $\beta$ -D-xylo-	-8.8	+17.5

<sup>a</sup> Results of W. G. Overend, C. W. Rees, and J. S. Sequeira, *J. Chem. Soc.*, 3429 (1962). <sup>b</sup> Unpublished result of A. A'Court.

are given the entropies of activation for the acid-catalyzed hydrolysis of a series of furanosides and the corresponding pyranosides. The contrast between the two sets of results is striking, and the simplest explanation of the negative values for the furanosides is that they react by an A2 mechanism, which would not be too surprising in view of the generally observed greater ease of nucleophilic attack on five-membered compared with six-membered rings.<sup>5</sup> The possibility that these negative entropies of activation result from an intramolecular nucleophilic attack by one of the hydroxyl groups is excluded by the observation that the entropy of activation for the hydrolysis of methyl  $\alpha$ -D-galactofuranoside (II) is similar to the others. With this furanoside, nucleophilic attack with inversion of con-



figuration by the hydroxyl groups at positions 2, 5, and 6 to form a three-, five-, or six-membered ring is prevented sterically. Thus the criterion of mechanism based on entropy of activation supports an A2 mechanism, but clearly confirmation of this by another criterion is desirable.

(5) See E. L. Eliel in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 121.

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Received June 28, 1965

### On the Mechanism for the Pyrolysis of Diborane

Sir:

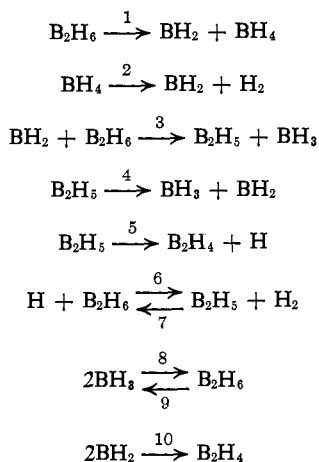
Nearly all of the reactions of diborane have been interpreted in terms of a mechanism involving the dissociation of diborane into two borane (BH<sub>3</sub>) molecules which are postulated as being the active species.<sup>1</sup>

(1) S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 5775 (1956).

As was recently pointed out,<sup>2</sup> some anomalies are created by the attempt to employ this basic mechanism universally. When applied to the thermal decomposition of diborane, for example,<sup>3-5</sup> this mechanism cannot satisfactorily explain the presence of the BH<sub>2</sub> radical,<sup>6</sup> the change in order with temperature,<sup>7</sup> and the large kinetic isotope effect in the production of hydrogen.<sup>8</sup>

The purpose of this note is to point out that the experimental data on this system, including the three points just mentioned, no longer support a mechanism with borane as the active species. It is shown here that a radical chain mechanism is kinetically feasible and qualitatively superior to the borane mechanism.

The mass spectrometric identification of BH<sub>2</sub> in the pyrolysis of diborane<sup>6</sup> provides the basis for the new mechanism which may be written as<sup>9</sup>

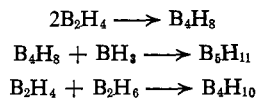


the net reaction being



It may be noted that the last equation, with the exception of H<sub>2</sub>, does not correspond to the observed final products, B<sub>4</sub>H<sub>10</sub>, B<sub>5</sub>H<sub>9</sub>, B<sub>5</sub>H<sub>11</sub>, B<sub>10</sub>H<sub>14</sub>, and polymer.<sup>10</sup> B<sub>2</sub>H<sub>4</sub> is undoubtedly very unstable, being unobserved up to the present time, and thus in order to describe the initial stages of the pyrolysis, it is sufficient to postulate that B<sub>2</sub>H<sub>4</sub> rapidly condenses with itself or other species to produce the observed products.

It is possible to be more specific as, for example, reactions such as



could account for B<sub>4</sub>H<sub>10</sub> and B<sub>5</sub>H<sub>11</sub>.<sup>3,4</sup> However, these and other possible steps will remain conjectural

(2) M. E. Garabedian and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 176 (1964).

(3) J. K. Bragg, L. V. McCarty, and F. J. Norton, *ibid.*, **73**, 2134 (1951).

(4) K. Borer, A. B. Littlewood, and C. S. Phillips, *J. Inorg. Nucl. Chem.*, **15**, 316 (1960).

(5) R. P. Clarke and R. N. Pease, *J. Am. Chem. Soc.*, **73**, 2132 (1951).

(6) T. P. Fehlner and W. S. Koski, *ibid.*, **86**, 2733 (1964).

(7) G. B. Skinner and A. D. Snyder, paper presented at the meeting of the American Institute of Aeronautics and Astronautics, Dec. 1963.

(8) R. E. Enrione and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **18**, 103 (1961).

(9) It may be noted that this mechanism is very similar to the Rice-Herzfeld mechanism for the pyrolysis of hydrocarbons.

(10) J. R. Morrey, A. B. Johnson, Y. Fu, and G. R. Hill, *Advances in Chemistry Series*, No. 32, R. F. Gould, Ed., American Chemical Society, Washington, D.C., 1961, p. 157.

until more data on stoichiometry, initial product distribution, and intermediates become available.

Using a conventional stationary-state treatment for the intermediate species, H, BH<sub>2</sub>, BH<sub>3</sub>, BH<sub>4</sub>, and B<sub>2</sub>H<sub>5</sub> (H, BH<sub>4</sub>, and B<sub>2</sub>H<sub>5</sub> as yet are unreported in the pyrolysis although B<sub>2</sub>H<sub>5</sub> has been postulated as an active species in the photolysis<sup>11</sup>), one may obtain the equation

$$R = k_1[\text{B}_2\text{H}_6] + \frac{k_5 k_3}{k_4} \left( \frac{k_1}{k_{10}} \right)^{1/2} [\text{B}_2\text{H}_6]^{3/2}$$

where  $R$  is the reaction rate ( $-d[\text{B}_2\text{H}_6]/dt = d[\text{H}_2]/dt = d[P_r]/dt$ , where  $P_r$  = total pressure). For long chains, the first term is negligible, and this equation agrees with the observed kinetics.<sup>3,4,12</sup>

The thermochemical data on this system are meager but as may be seen are consistent with this mechanism. If one reasonably assumes that  $D(\text{H}_3\text{B}-\text{BH}_3)^{13} = 37$ ,<sup>14</sup>  $D(\text{BH}_2-\text{H}) \approx D(\text{B}_2\text{H}_5-\text{H}) = 74$ ,<sup>3</sup>  $D(\text{H}_2\text{B}-\text{BH}_2) = 80$ ,<sup>15</sup> and  $D(\text{H}-\text{H}) = 104$ ,<sup>16</sup> then  $\Delta H_3 = 0$ ,  $\Delta H_5 = 31$ ,  $\Delta H_4 = 37$ , and  $\Delta H_6 = -30$ . Applying Semenov's rule,<sup>17</sup> one estimates  $E_3 = 12$  and  $E_6 = 4$  which in turn yields  $E_7 = 34$ . Assuming that the reverse of reactions 4 and 5 have negligible activation energies<sup>18</sup> yields  $E_4 = 37$  and  $E_5 = 31$ .

The experimental activation energy is given by the equation

$$E_{\text{exptl}} = E_5 + E_3 - E_4 + 1/2(E_1 - E_{10})$$

Inserting  $E_3$ ,  $E_4$ , and  $E_5$  from above and the average observed value of  $E_{\text{exptl}} = 28$ ,<sup>3,4</sup> and assuming  $E_{10}$  is negligible,<sup>18</sup> yields  $E_1 = 44$ . This is a reasonable value.

The experimental frequency factor is given by the equation

$$A_{\text{exptl}} = \frac{A_5 A_3}{A_4} \left( \frac{A_1}{A_{10}} \right)^{1/2}$$

and the observed value of  $A_{\text{exptl}}$  as calculated from the rate constant and activation energy for the reaction is about  $6 \times 10^{11}$  (l./mole)<sup>1/2</sup> sec.<sup>-1</sup>.<sup>3</sup> Using  $A_3 = A_4 = 10^{13}$  sec.<sup>-1</sup>,  $A_5 = 10^8$  l./mole sec.,  $A_{10} = 10^{11}$  l./mole sec., yields  $A_1 = 10^{18}$  sec.<sup>-1</sup>. Although this is a large value for a unimolecular decomposition it is not uniquely so<sup>19</sup> and is not an impossible value for this reaction.

The condition of long chains requires that  $k_5 k_3 / k_4 > (k_1 k_{10} / [\text{B}_2\text{H}_6])^{1/2}$ . For a pressure of diborane of 76 torr and temperatures up to 400°K., one can calculate that  $k_5 k_3 / k_4 > 10(k_1 k_{10} / [\text{B}_2\text{H}_6])^{1/2}$ . At temperatures above 500°K., however, this condition would no longer hold and, consequently,  $k_1[\text{B}_2\text{H}_6]$  would become the leading term in the rate equation. Interestingly enough, a shock tube study<sup>7</sup> on the pyrolysis in the temperature range 600–700°K. yields first-order kinetics.

(11) W. C. Kreye and R. A. Marcus, *J. Chem. Phys.*, **37**, 419 (1962).

(12) As the mechanism only attempts to describe the initial stages of pyrolysis (before the discontinuity in the rate) the data in ref. 5 are not considered.

(13)  $D$  refers to bond dissociation energy,  $\Delta H$  to change in enthalpy, and  $E$  to activation energy. Energies are given in kcal./mole.

(14) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **87**, 409 (1965).

(15) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 2173 (1961).

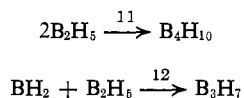
(16) T. L. Cottrell, "The Strengths of Chemical Bonds," Butterworth & Co. Ltd., London, 1958.

(17) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Pergamon Press, New York, N. Y., 1958.

(18) M. Szwarc, *Chem. Rev.*, **47**, 75 (1950).

(19) S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

In order for (10) to be the predominant terminating step,  $R_{10}$  must be larger than the rates of the other possible termination steps which are



For the same conditions as above  $R_{10}$  will be greater than  $R_{11}$  and  $R_{12}$  only if these last reactions have small steric factors and nonzero activation energies. This is not unreasonable as the reactions are not simple radical recombinations as is (10). Because the products  $B_3H_7$  and  $B_4H_{10}$  have relatively complex structures,<sup>20</sup> considerable rearrangement and orientation is required in the respective activated complexes.

As mentioned above, the experimental facts which are perplexing in terms of the borane mechanism can be explained in the framework of this mechanism. The facts that the pyrolysis involves both  $BH_2$  and  $BH_3$  and that the order changes with temperature have already been discussed. If one of the reactions of  $B_2H_4$  is the rapid condensation to polymer with the elimination of hydrogen, the mechanism accounts for the fact that polymer formation occurs to a significant extent even at relatively low fractions of diborane decomposition.<sup>10</sup> If one allows (5) to be reversible, the inhibition by hydrogen of the reaction<sup>5</sup> and of the formation of polymer<sup>21</sup> follows naturally. To calculate the rate expression, however, would require explicit knowledge of the fate of  $B_2H_4$  and thus is not included here.

An important point in favor of this mechanism is that the explanation of the large normal kinetic isotope effect ( $k_H/k_D = 5$ ) observed in the production of hydrogen from diborane<sup>8</sup> also follows readily. It is quite clear that the main contribution to the isotope effect will be from step 5, a unimolecular decomposition involving the rupture of a boron-hydrogen bond. If approximations suitable for isotopic hydrogen in heavy molecules are made and if it is assumed that all three hydrogen vibrations are lost on passing into the transition state,<sup>22</sup> then taking the B-H stretching frequency =  $2500\text{ cm}^{-1}$  and the two bending frequencies together =  $2000\text{ cm}^{-1}$ ,  $k_H/k_D = 5$  in excellent agreement with the experiment.

Perhaps as important is the fact that this mechanism suggests a starting point for an explanation of the ambiguous results on the reaction of diborane with ethylene<sup>2,23</sup> and on other systems.<sup>2</sup> One must conclude that on the basis of presently available data, the radical chain mechanism proposed here is an appealing one. One cannot, however, eliminate the borane mechanism as a parallel path although it at least seems clear that the latter mechanism does not predominate.

(20) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

(21) T. P. Fehlner and W. S. Koski, *J. Am. Chem. Soc.*, **86**, 1012 (1964).

(22) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press, New York, N. Y., 1960.

(23) A. T. Whatley and R. N. Pease, *J. Am. Chem. Soc.*, **76**, 835 (1954).

T. P. Fehlner

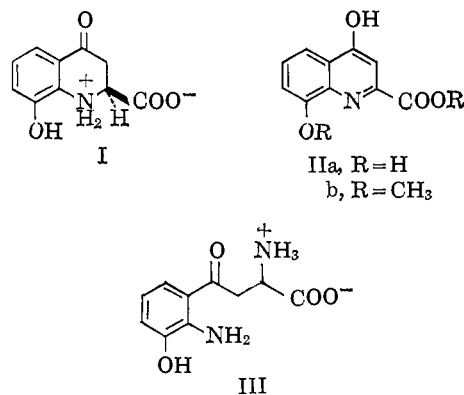
Department of Chemistry, University of Notre Dame  
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Received July 16, 1965

## A New L- $\alpha$ -Amino Acid from Lepidoptera

Sir:

Cold methanol extraction of light yellow pigmented areas in the wings and bodies of a large number of Ithomid and Heliconian butterflies<sup>1</sup> has yielded a new L- $\alpha$ -amino acid (0.05–0.7 mg./insect) for which structure I (L-8-hydroxy-1,2,3,4-tetrahydro-4-oxoquinaldic acid = L-dihydroxanthurenic acid) has been established. A representative of a new class of substituted quinoline derivatives,<sup>2</sup> I also presents the interesting possibility (presently under investigation) of forming with xanthurenic acid (IIa) an oxidation-reduction couple in insect metabolic processes.<sup>3</sup>



The crystalline pigment, m.p.  $185\text{--}190^\circ\text{ dec.}$ ,  $[\alpha]^{20D} -45^\circ$  ( $c$  0.9, MeOH),  $+18^\circ$  ( $c$  0.9, MeOH-HCl), ninhydrin positive, showed in the infrared (KBr) bands typical for a zwitterionic  $\alpha$ -amino acid ( $3000\text{--}2000$ ,  $1610$ ,  $1540$ , and  $1400\text{ cm}^{-1}$ ) and a highly conjugated carbonyl (vinylogous amide, comparable to  $\gamma$ -pyridone;  $1630\text{ cm}^{-1}$ ). Acetylation gave a mixture showing absorption for phenol acetate ( $\nu_{\text{max}}^{\text{CHCl}_3}$   $1760$  and  $1210\text{ cm}^{-1}$ ); methylation afforded an oil showing (as film) absorption for saturated methyl ester ( $1740$  and  $1175\text{ cm}^{-1}$ ), aromatic methoxyl ( $2870$ ,  $1450$ ,  $1360$ , and  $1030\text{ cm}^{-1}$ ), and  $\gamma$ -pyridone type groupings ( $3380$ ,  $1650$ , and  $1550\text{ cm}^{-1}$ ). The n.m.r. spectrum ( $100\text{ Mc.}$ ,  $\text{CD}_3\text{COOD}$ )<sup>4</sup> revealed the presence of three adjacent aromatic protons ( $\delta$  7.30, doublet; 6.93, doublet; and 6.58, triplet, all  $J$  values 8 c.p.s.) and three additional protons as deshielded methylene ( $\delta$  3.65) and methine ( $\delta$  4.5) groups. The ultraviolet

(1) These are of subfamily *Ithomiinae* and genus *Heliconius* of subfamily *Heliconiinae*, two large neotropical groups of the family *Nymphalidae*; almost all members of these groups examined stored the amino acid in body and wings. A distantly related nymphalid, the female of *Catonephele numilia* (a mimic of *Heliconius sara*), also stored the pigment in the fore wings, and other related species stored a closely related compound of as yet uncertain structure. See also footnote 3. Complete distribution data for the pigment will be presented along with taxonomic comments in a paper to the *Journal of the Lepidopterists' Society*.

(2) Although dihydrocarbostyryl- and dihydroisocarboxystyrylcarboxylic acids have been reported, no mention was noted in the literature of any derivative of any 2,3-dihydro-4(1H)-quinolonecarboxylic acid.

(3) The pigment I in an insect is readily detectable by its solubility in cold MeOH, bright yellow fluorescence,  $R_f$  on paper chromatography (0.45 in the system  $\text{BuOH-HOAc-H}_2\text{O}$  4:1:5), and characteristic ultraviolet spectrum (in purer samples; see below). Thus, I appeared to be present in small quantities in the bodies and/or wings of a wide variety of Lepidoptera which did not specifically store it in pigmented areas. Xanthurenic acid also seemed to be present in small quantities in many species and has already been reported in the silkworm, *Bombyx mori* (K. Inagama, *Nippon Sanshigaku Zasshi*, **24**, 295 (1955)) and *Drosophila* (Y. Umebachi and K. Tsuchitani, *J. Biochem.* (Tokyo), **42**, 817 (1955)).

(4) The author is grateful to Dr. Lois Durham of Stanford University, Calif., for the n.m.r. measurements. Values are in  $\delta$  (p.p.m.) from tetramethylsilane as internal reference.