

acrolein, methyl vinyl ketone, or methyl acrylate, respectively. Each of these products possesses a conjugated system $C=C-C=O$ and therefore more resonance stabilization than the corresponding products from the alkylcyclobutanes. From a consideration of enthalpies of hydrogenation corrected for polar and hyperconjugative effects, Kreevoy and Taft¹² have reported that the resonance energy of an unsaturated ester ($CH_3CH=CHCO_2R$) is 5.7 kcal./mole which is only slightly smaller than the value for crotonaldehyde.¹³ They found that this conclusion was in accord with molecular orbital calculations. In α,β -unsaturated aldehydes, ketones, and esters the lowering of the $C=O$ and $C=C$ infrared frequencies (with respect to those in the corresponding saturated molecules) is ascribed to conjugation, and the frequency shift for unsaturated esters is smaller than the lowering for aldehydes and ketones.¹⁴

(12) M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **79**, 4016 (1957).

(13) For a different point of view see G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 84 and 483.

Ingold¹⁵ has concluded that for $ROC=O$ the relative mesomeric effect of the whole substituent group is less than that for $HC=O$. On this same basis $CH_3-C=O$ would be expected to lie between $HC=O$ and $CH_3OC=O$ because CH_3 is regarded as more electron-releasing than H. In view of the various experimental results and discussions appearing in the literature, the fact that the rate constants for the cyclobutane derivatives decrease in the order $HC=O > CH_3C=O > CH_3OC=O$ is not unexpected.

Acknowledgment.—The authors wish to thank Mr. Carl Whiteman for making the infrared measurements and the least squares analysis, Dr. Jack A. Kampmeier for helpful discussions, and Dr. R. Whiteoak for advice and assistance in the preparation of methyl cyclobutanecarboxylate. Grateful acknowledgment is made also to the General Railway Signal Co. for the use of the IBM 650 computer.

(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 136, 155, 181 W. H. T. Davison and G. R. Bates, *J. Chem. Soc.*, 2607 (1953).

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry" Cornell University Press, Ithaca, N. Y., 1953, pp. 76–78.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES 7, CALIF.]

The Kinetics of the Decomposition of BH_3CO and the Bond Dissociation Energy of B_2H_6 ¹

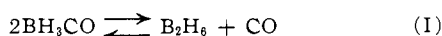
By MICHAEL E. GARABEDIAN AND SIDNEY W. BENSON

RECEIVED NOVEMBER 17, 1962

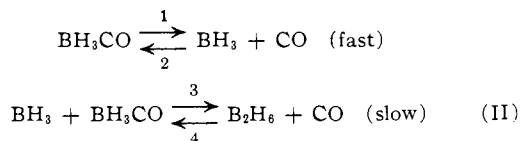
A reanalysis of the kinetic data on BH_3CO decomposition to give $1/2 B_2H_6 + CO$ is shown to be in excellent agreement with the original mechanism, II in text. By integration of the exact, steady-state rate law and fitting to the data it is shown that $k_3/k_2 < 10^{-8}$ so that the assumption that the first step is at equilibrium is an excellent one. The best fit to all of the data yields (units of sec^{-1}): $\log(k_1k_3/k_2) = 13.58 - 26,750/4.575T$. Together with the observed data on the equilibrium this gives (units of l./mole-sec.): $\log k_4 = 8.32 - 17,650/4.575T$. From the entropy change in step 1, $A_3 = 10^{9.16}$ l./mole-sec. Reasonable estimates of A_1 and A_2 are $10^{14.4} sec^{-1}$ and 10^9 l./mole-sec. It is shown that these values are consistent with a bond dissociation energy of B_2H_6 of 28 kcal. only if we assign E_2 the unlikely value of 4.9 kcal./mole. They do, however, fix an upper limit $D(B_2H_6) \leq 38.3$ kcal./mole. A lower limit is provided by fixing a value for the rate of recombination of BH_3 . If the latter has a rate constant of 10^{10} l./mole-sec., then this lower limit is 35 kcal./mole, while a value of 10^8 would yield 32 kcal./mole.

Introduction

Burg² has studied the kinetics and equilibrium in the system



He was able to show that the early stages of the decomposition could be fitted very closely by the mechanism



This mechanism was criticized by Bauer,³ who decided that it led to too high a bond energy for the B_2H_6 dissociation. He then proposed an alternative mechanism which we shall show is not satisfactory.

More recently, the system has been restudied spectrophotometrically⁴ at a somewhat higher temperature and with varying amounts of different added gases including CO, H_2 , and B_2H_6 . It was confirmed that CO was a very effective inhibitor while H_2 and B_2H_6 were without effect. Unfortunately these data of Fu and Hill do not appear to fit their proposed second-order

mechanism and the analysis which they made was erroneous.⁵

In view of this somewhat unsatisfactory situation it was felt desirable to re-examine the work that had been done and attempt to reconcile the various conflicting interpretations. On the basis of such an examination we shall show that the initial criticisms were not justified and that in fact Burg's mechanism is in reasonable agreement with all of the available data on the system.

Mechanism

If we apply the usual "steady"-state treatment to the mechanism II and ignore for the moment the back reaction 4 we find for the rate law

$$-\frac{d(BH_3CO)}{dt} = \frac{2k_1k_3(BH_3CO)^2}{k_2(CO) + k_3(BH_3CO)} \quad (1)$$

Using the stoichiometry of the over-all reaction I, we set $Z = \Delta(BH_3CO)/(BH_3CO)_0 = (CO)/(BH_3CO)_0$ = fraction of reaction. On substitution into eq. 1 we obtain a standard equation whose integrated form is

$$2K_{1,2}k_3t = \frac{Z}{1-Z} + (1 - K_{3,2}) \ln(1 - Z) \quad (2)$$

where we use $K_{1,2} = k_1/k_2$ and $K_{3,2} = k_3/k_2$.

The RHS of this equation is virtually insensitive to Z in the range $0 \leq Z \leq 0.3$ if $K_{3,2}$ should be very small

(5) Dr. G. R. Hill, private communication, reports an error in their integration of the rate law.

(1) This work has been supported by grants from the U. S. Atomic Energy Commission and the National Science Foundation.

(2) A. B. Burg, *J. Am. Chem. Soc.*, **74**, 3482 (1952); **59**, 780 (1937).

(3) S. H. Bauer, *ibid.*, **78**, 5775 (1956).

(4) Y. C. Fu and G. R. Hill, *ibid.*, **84**, 353 (1962).

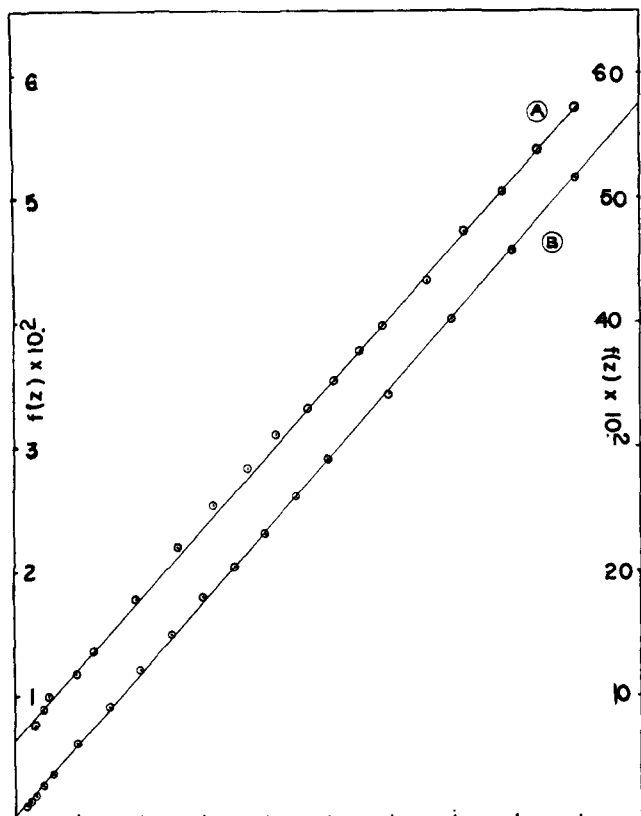


Fig. 1.—Curve A, $f(Z)$ expanded ($K_{3.2} \neq 0$), corresponds to the left abscissa ordinate, $t/Z \times 10^{-2}$ running from 1 to 11. Curve B, $f(Z)$ exact ($K_{3.2} = 0$), corresponds to the right abscissa and has for an ordinate t running from 0 to 100; $k_{\text{exp}}^A = 47.2 \times 10^{-8} \text{ sec.}^{-1}$; $k_{\text{exp}}^B = 48.4 \times 10^{-8} \text{ sec.}^{-1}$.

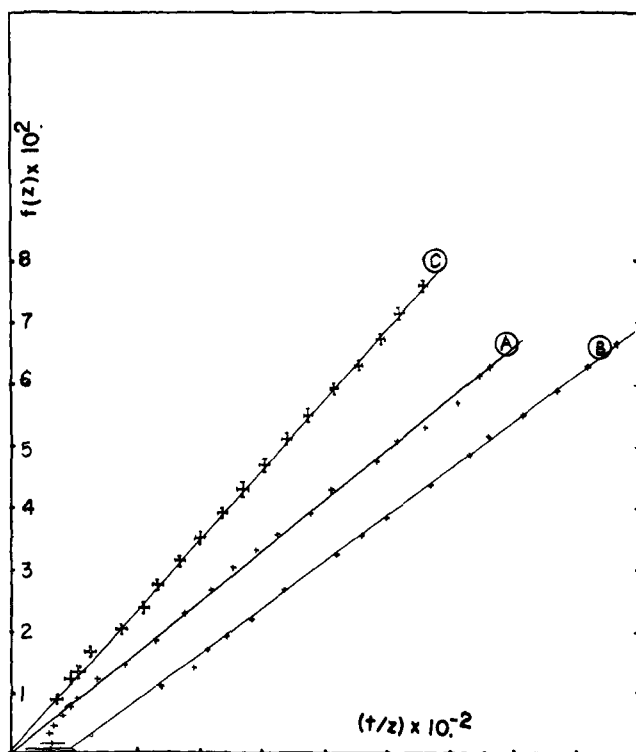


Fig. 2.—A is at 13.28° and $(\text{BH}_3\text{CO})_0$ of 71.43 mm., ordinate from 0 to 50; B, 23.42° and $(\text{BH}_3\text{CO})_0$ of 79.34 mm., ordinate from -1 to 9; C, 29.69° and $(\text{BH}_3\text{CO})_0$ of 27.69 mm., ordinate from 0 to 4; $k_{\text{obsd}}^A = 13.8 \times 10^{-8} \text{ sec.}^{-1}$, $k_{\text{obsd}}^B = 63.95 \times 10^{-8} \text{ sec.}^{-1}$, $k_{\text{obsd}}^C = 237.2 \times 10^{-8} \text{ sec.}^{-1}$. All are the expanded form of $f(Z)$.

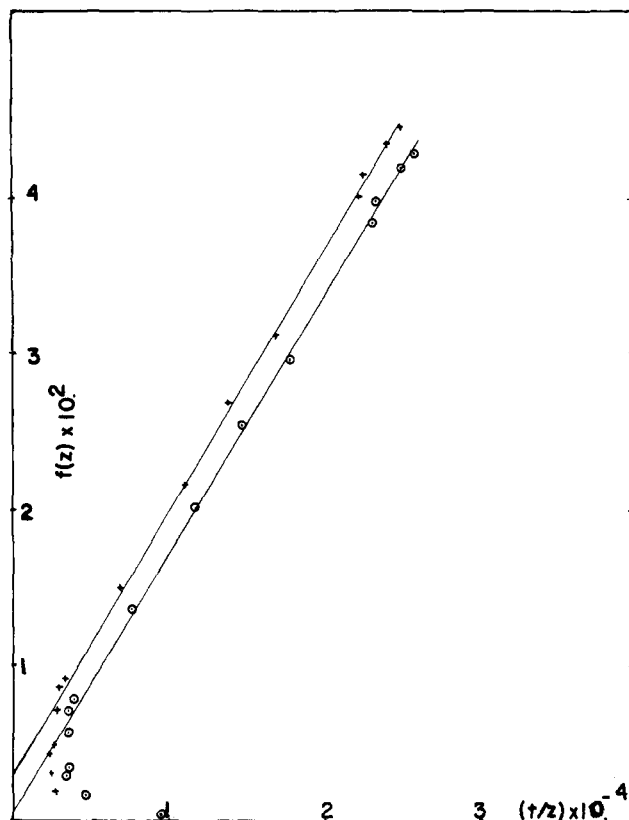


Fig. 3.—Burg's original 0° run (represented by \odot) and the run assuming a 0.1-mm. error in $P(\text{BH}_3\text{CO})_0$ (represented by $+$): $k_{\text{obsd}}^\odot = 1.40 \times 10^{-8} \text{ sec.}^{-1}$; $k_{\text{obsd}}^+ = 1.42 \times 10^{-8} \text{ sec.}^{-1}$; plotted by the expanded form of $f(Z)$.

which is the actual case.⁶ On expanding the two terms in the RHS of eq. 2 in powers of Z we find

$$2K_{1.2}k_3t = Z^2/2 + 2Z^3/3 + \dots + (n-1)Z^n/n + \dots + K_{3.2}(Z + Z^2/2 + \dots) \quad (3)$$

and for $Z < 0.2$, $K_{3.2} < Z$

$$2K_{1.2}k_3t \sim Z^2/2 + 2Z^3/3 + K_{3.2}(Z)$$

This equation can be plotted in two ways depending on the assumptions made. If we follow Burg and assume that $K_{3.2}$ is negligible, a plot of $f(Z) = Z^2/2 + 2Z^3/3$ vs. t yields a straight line of slope $2K_{1.2}k_3$ with an intercept of zero. But if $K_{3.2}$ is not considered negligible, a plot of $Z/2 + 2Z^2/3$ vs. t/Z yields a straight line of slope $2K_{1.2}k_3$ with an intercept of $-K_{3.2}$. Both types are illustrated in Fig. 1 for the same data.

Figure 2 shows three typical plots of $Z/2 + 2Z^2/3$ vs. t/Z , taken from Burg's raw data. In Fig. 3 we show the similar plot for the 0° run used by Bauer in his analysis. The circles show the original data, while the crosses show the same data plotted with the supposition that the extrapolated pressure reading at $t = 0$ was in error by 0.1 mm. We see that by taking $(\text{BH}_3\text{CO})_0 = 74.4$ mm. instead of 74.5 mm., that the early drift is considerably reduced while the slope is unchanged.

The t/Z plots spread out the early points for which the accuracy is least and compress the later points for which the accuracy is greatest, but the opposite is true of the t vs. $f(Z)$ plots. In each case the t/Z plots were compared with the t vs. $f(Z)$ plots. The results of this comparison showed that in all but one case the difference in $K_{1.2}k_3$ was less than 4%. Since this is well within the experimental error, we have chosen the

(6) Burg's original equation was identical with eq. 2 if we set $K_{3.2} = 0$.

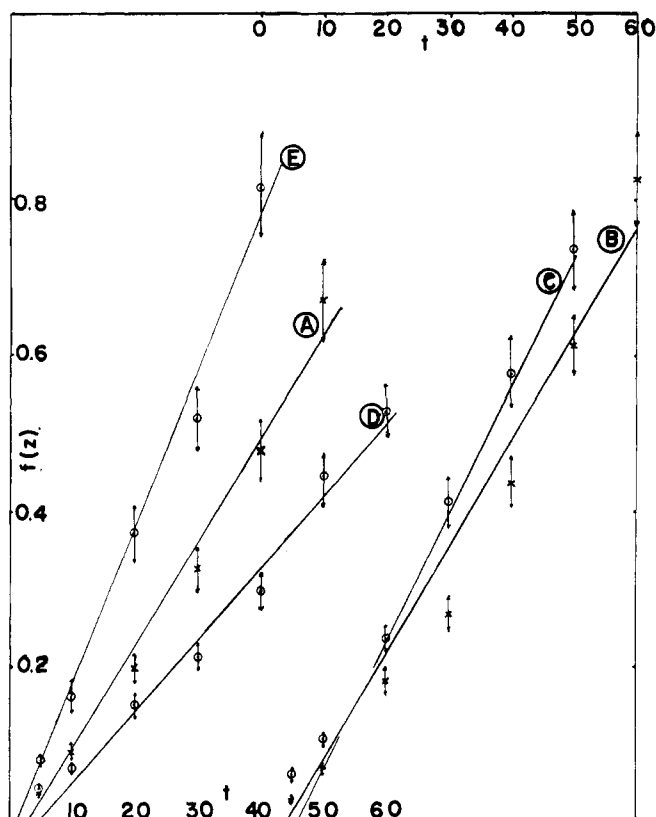


Fig. 4.—Plot of Fu and Hill's data in the exact form of $f(Z)$ for experiments 6-E, 7-A, 8-B, 11-C, and 13-D. This was done assuming a 3% error in the pressure readings. Note: The BC₀ in no. 8 was taken as 19.2 mm. This was done in order to obtain better fit to the curve in view of the fact that the majority of the points in 8 did fit. All of the other data fit well.

former method of representing the data. We have done t/Z type plots for all of the raw data of Burg and we find that the intercept is in every case either positive, or if negative, ≥ -0.0010 or, within the limits of experimental error it is effectively zero.

It should be emphasized that the pressure measurements do not give a very precise method of following the rate. Since the over-all stoichiometry of eq. 1 is 1.5 moles of product per mole of reactant, the uncertainty in Z is twice the uncertainty in the difference in two pressure readings. Since most of Burg's data are confined to 15% reaction and his precision of pressure measurement is ± 0.02 mm. at a total pressure of ~ 60 mm., his expected precision in Z is about $\pm 10\%$ at 1% decomposition and $\pm 1\%$ at 10% decomposition. Since the integrated form of the equation has Z^2 as the leading term because $K_{3,2} \ll 1$, this means that the points in the plot have a precision in the Z function of $\pm 20\%$ at 1% decomposition and $\pm 2\%$ at 10% decomposition. For this reason we are not inclined to put as much weight on the early points as Bauer did.

It has been suggested that reactions 1 and 2 might be in a pressure dependent region. If we make the extreme assumption that they are at the low pressure end of their pressure dependence so that $k_1 = k_1'(M)$ and $k_2 = k_2'(M)$, then the rate law becomes

$$-\frac{d(\text{BH}_3\text{CO})}{dt} = \frac{2k_1k_3(\text{BH}_3\text{CO})^2(M)}{k_2(\text{CO})(M) + k_3(\text{BH}_3\text{CO})} \quad (4)$$

Now in Burg's experiments, no added gases were employed so that (M) could be replaced by (BH_3CO) . In this case eq. 4 reduced to

$$-\frac{d(\text{BH}_3\text{CO})}{dt} = \frac{2k_1k_3(\text{BH}_3\text{CO})^2}{k_2(\text{CO}) + k_3} \quad (5)$$

If we again use the stoichiometry to substitute Z , we find that we obtain an integrated equation, identical in functional form with 2, so that the data do not lend themselves to a test of this suggestion. In any case, we see that such pressure dependence can only be observed if $K_{3,2}/(\text{CO})$ is appreciable; otherwise the pressure dependence of steps 1 and 2 cancel. The best experimental evidence on this point, however, is the finding by Fu and Hill that H_2 had no effect on the rate. We therefore conclude that there is no experimental support for the hypothesis of a pressure dependence for steps 1 and 2.

Fu and Hill chose to plot all of their data as if the reaction were purely second order in BH_3CO , thus neglecting the very important CO inhibition. The result is that all of their plots are strongly curved, concave to the time axis. If we accept Burg's equation, it is clear that Fu and Hill's rates are starting out very fast and diminishing as CO builds up. Their experiments with initial CO are more nearly second order because the added CO now masks the importance of liberated CO. In Fig. 4 we show five representative plots of the data of Fu and Hill, plotted in the form of t vs. $f(Z)$. It can be seen that they give a reasonable fit to this form of the equation. It is noted that if a correction is made for the H_2 produced, assuming a reaction between BH_3CO and B_2H_6 , the agreement is greatly improved.

In the presence of added CO, eq. 1, now for convenience, neglecting $K_{3,2}$, becomes

$$-\frac{d(\text{BH}_3\text{CO})}{dt} = \frac{2k_1k_3}{k_2} \frac{(\text{BH}_3\text{CO})^2}{(\text{CO})_0 + (\text{BH}_3\text{CO})_0 - (\text{BH}_3\text{CO})} \quad (6)$$

or, in integrated form

$$2K_{1,2}k_3t = \frac{Z}{1-Z} \left(1 + \frac{C_0}{B_0}\right) + \ln(1-Z) = F(Z) \quad (7)$$

where C_0/B_0 = the ratio of initial CO to initial BH_3CO .

Now expanding the RHS in powers of Z

$$2K_{1,2}k_3t = \frac{C_0}{B_0}(Z + Z^2 + Z^3) + \frac{Z^2}{2} + \frac{2}{3}Z^3 \quad (8)$$

In the experiments of Fu and Hill with added CO, C_0/B_0 was in the range 0.3 to 1.3, while Z was followed to 0.50 so that the dropping of the quartic terms in eq. 8 can produce up to a 10% error at the final stages of reactions. For added CO, eq. 7 can be used directly, and in Fig. 5 we show the data of Fu and Hill plotted after eq. 7. As can be seen, there is an excellent fit to the data.

We thus conclude that all of the published data are in agreement with the simple Burg mechanism all the way down to 0.3% conversion; at the lower values the experimental error obscures the meaning of the plotted points. Also, the reaction of BH_3 with CO is very rapid relative to its reaction with BH_3CO , even at ratios of $(\text{CO})/(\text{BH}_3\text{CO})$ of the order of 10^{-3} .

Rate Data

In Fig. 6 is shown an Arrhenius type plot of all of the experimental rate constants which are equal to $K_{1,2}k_3$. It can be seen that the solid line represents a very good fit to the lower temperature data of Burg and the high temperature data of Fu and Hill. It is evident that the latter is more scattered than the former. The Arrhenius parameters for the solid line are

$$\log(K_{1,2}k_3) = 13.58 - 26,750/4,575T \quad (9)$$

where the units of $K_{1,2}k_3$ are sec.^{-1} . The uncertainties are ± 1 kcal./mole in the activation energy and a corresponding ± 0.7 in the $\log(A_{1,2}A_3)$. This is reasonably close to Burg's parameters of 27.5 kcal. and $\log(A_{1,2}A_3) = 14.09$.

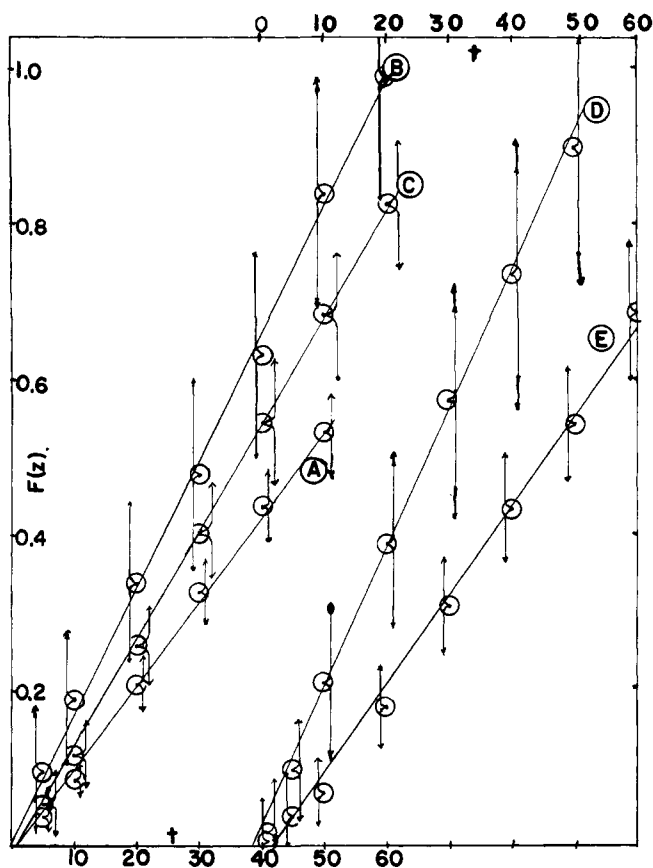
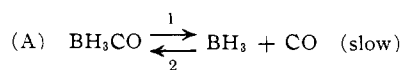


Fig. 5.—Fu and Hill's data, assuming 3% error in PBC , for experiments 18-E, 19-D, 20-B, 21-C, and 22-A. Ordinate at bottom for A, B, C, at top for D and E. The errors are shown displaced.

From Shepp and Bauer's data⁷ for the standard entropy change in reaction 1 of 33.2 gibbs/mole we calculate $A_1/A_2 = 10^{7.26}$ atm. = $10^{5.42}$ moles/l. so that $A_3 = 10^{8.16}$ l./mole-sec. This is an altogether reasonable value for the displacement reaction 3. Since the over-all standard entropy change in the decomposition is observed¹ to be 32.5 gibbs/mole we can calculate that $A_1A_3/A_2A_4 = 10^{5.26}$ mole/l. Combining this with A_1A_3/A_2 we find that $A_4 = 10^{8.32}$ l./mole-sec. which is again a quite reasonable value for the attack of CO on B_2H_6 . It is to be noted that this last reaction is a Walden inversion since the B atom goes from one tetrahedral configuration in B_2H_6 to an inverted type in BH_3CO . From the thermodynamics we find $E_4 = 17.7$ kcal./mole.

While there is not much basis for estimating either A_1 or A_2 , it is very likely that the latter is in the range of $10^{9.0 \pm 0.5}$ l./mole-sec. This then yields the value $10^{14.42}$ sec.⁻¹ for A_1 , a value which would be consistent with a not-too-loose transition-state complex. A minimum value of A_2 would be about 10^8 l./mole-sec. which would put A_1 at $10^{13.42}$ sec.⁻¹. If we use the higher value of A_2 together with the derived value of $A_3 = 10^{8.16}$ l./mole-sec., then the observation that $K_{3.2} \leq 10^{-3}$ at room temperature immediately puts a lower limit on $E_3 - E_2 \geq 3.02$ kcal. This then puts an upper limit on E_1 of $26.75 - 3.02 = 23.73$ kcal./mole.

Bauer has suggested an alternative mechanism: Using our notation



(7) A. Shepp and S. H. Bauer, *J. Am. Chem. Soc.*, **76**, 265 (1954).

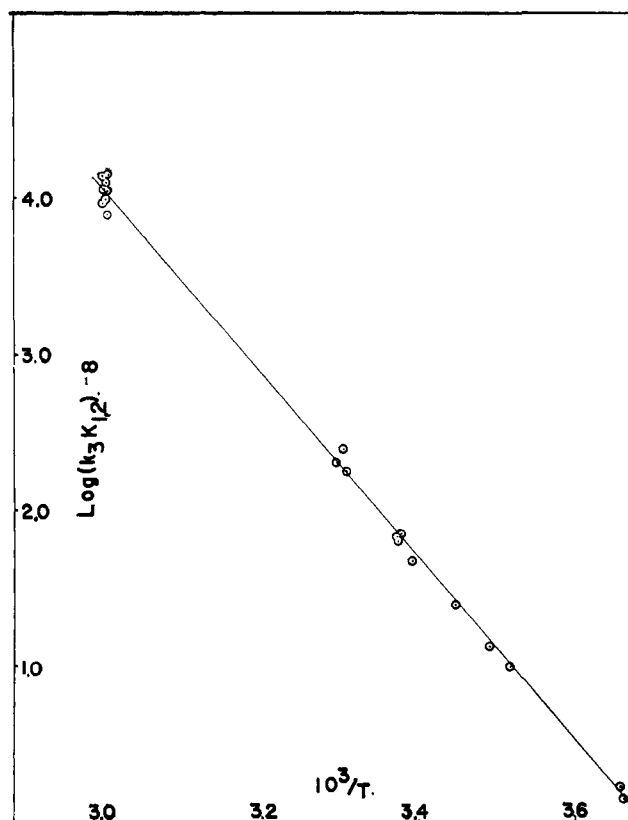
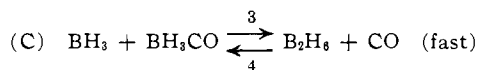
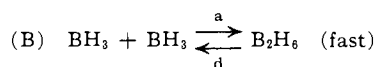


Fig. 6.—The Arrhenius plot for all available data: $\log k_1k_3/k_2 = 13.58 - 26,750/4.575T$ (sec.⁻¹.)



Following Bauer's assumptions for the early stages of the reaction⁸ we are faced with the situation that reaction 4 can only become operative after B_2H_6 is formed. If we start with pure BH_3CO this can only happen *via* reaction B since reactions 2 and 3 cannot take part in the formation of B_2H_6 or the disappearance of BH_3 .

We find that the time to reach a steady state of BH_3 in the system is long compared to the time for the initial few per cent decomposition of BH_3CO . This cannot be correct, for if it were, the steady-state treatment presented here could not yield straight line curves over the initial 10% reaction as it has for the majority of Burg's data.

Also, if we allow these assumptions and neglect to examine the steady-state condition, we can represent the rate of disappearance of BH_3CO in the initial stages as

$$-d(\text{BH}_3\text{CO})/dt = k_1(\text{BH}_3\text{CO}) - k_4(\text{B}_2\text{H}_6)(\text{CO})$$

which can be written as

$$-d(\text{BH}_3\text{CO})/dt = k_1(\text{BH}_3\text{CO}) \left[1 - K_{3.2} \frac{(\text{B}_2\text{H}_6)(\text{CO})}{K_{\text{eq}}(\text{BH}_3\text{CO})} \right] \quad (10)$$

where $K_{\text{eq}} = K_{1.2}K_{3.4}$.

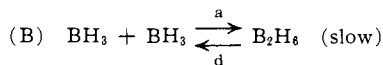
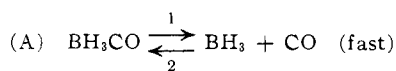
Under the conditions where the rate measurements were made, the back reaction is entirely negligible⁹; since we have shown that $K_{3.2}$ is approximately zero, only the first term on the RHS of eq. 10 is needed to describe the rate. This expression is in obvious conflict with the observed facts. It predicts no effect of

(8) These being: (1) step B is negligible; (2) $k_2(\text{BH}_3) \ll k_1(\text{B}_2\text{H}_6)$ and $k_3(\text{BH}_3) \ll k_4$.

(9) In all cases, from both Burg's and Hill's data, the reaction proceeded to a maximum of 6% toward equilibrium.

(CO) and shows a first-order dependence on (BH₃CO), neither of which is observed.

The other possible alternative mechanism is



which leads to

$$-\frac{d(\text{BH}_3\text{CO})}{dt} = 2 \frac{k_1^2}{k_2^2} k_a \frac{(\text{BH}_3\text{CO})^2}{(\text{CO})^2}$$

Upon integration it is found that the resulting expressions must be expanded for the same reasons given earlier.¹⁰ It leads to

$$Z^3 + \frac{3}{2} Z^4 = 2(k_1/k_2)^2 \frac{k_a}{(\text{BH}_3\text{CO})_0} t$$

Therefore, $[Z^3 + \frac{3}{2} Z^4]/2t$ should be a constant, but this is found to vary by a factor of six over an 11% conversion for the best available sets of data. One would also expect that the experiments of Fu and Hill with added CO would not agree with the Burg mechanism but this is certainly not the case (see Fig. 5).

If it is desired to include both terms in the rate, that is both mechanisms being operative, the resulting equation would be

$$\begin{aligned} -\frac{d(\text{BH}_3\text{CO})}{dt} &= k_B \frac{(\text{BH}_3\text{CO})^2}{(\text{CO})} (\text{BH}_3\text{CO})_0 + \\ &\quad \left(\frac{k_1}{k_2}\right)^2 \frac{k_a}{(\text{BH}_3\text{CO})} \frac{(\text{BH}_3\text{CO})^2}{(\text{CO})^2} \\ &= k_B (\text{BH}_3\text{CO})_0 \frac{(\text{BH}_3\text{CO})^2}{(\text{CO})} \left[1 + \right. \\ &\quad \left. \left(\frac{k_1}{k_2}\right)^2 \frac{k_a}{(\text{BH}_3\text{CO})_0^2 (\text{CO})} \right] \end{aligned}$$

The second term is a negligible correction at 0.3% conversion and it decreases in importance as (CO) increases. Therefore the first term describes the principal path of the reaction, but this is just the Burg mechanism.

The Bond Dissociation Energy of B₂H₆

The results to be presented are in conflict with previous estimates of the bond dissociation energy of B₂H₆ of approximately 28.4 ± 2 kcal., but we feel that the previous estimates are unreliable. In 1956,³ eight values for the number were arrived at which ranged from 25 to 38.4 kcal. and these were considered to be compatible with an estimate of 28.4 ± 2 kcal. Four of the systems studied yielded values of 38.0, 38.4, 33.0, and 33.5 kcal. for an upper limit of the bond dissociation energy; our treatment yields an upper limit of 38.3 kcal. But we are able to arrive at a lower limit of 32.5 kcal. within the realm of our assumptions. It should be pointed out that in the authors' opinion this is the only system of those studied by Bauer where there is sufficient experimental evidence over a sufficient range of conditions to support a homogeneous mechanism.

Some comment on the conclusiveness of earlier results seem to be in order. In the first place, there is no rigorous method of obtaining $\Delta H_{\text{diss}}(\text{B}_2\text{H}_6)$ from thermochemical data and any method which employs the additivity relations of bond energies cannot be considered very reliable, since they are known to be unreliable.¹¹

The kinetic arguments which were used to support the value of 28.4 ± 2 kcal. for $\Delta H_{\text{diss}}(\text{B}_2\text{H}_6)$ are all based on the conjecture that the B₂H₆ ⇌ 2BH₃ equi-

librium is established and that it is done so homogeneously. However, in none of the cases cited³ is there any criterion for whether or not this equilibrium is established either homogeneously or heterogeneously. If it is established heterogeneously, then none of the conclusions would follow, for none of the criteria are applicable. In fact, we believe that in many of the systems cited this equilibrium is established heterogeneously. The over-all reaction would still appear to be independent of the surface to volume ratio since in most cases the slow step is presumed to be not the B₂H₆ ⇌ 2BH₃, but rather the next step, the attack of BH₃ on the added reactant.

In particular, reactions involving the formation or decomposition of a solid (PH₃ + B₂H₆ and Me₂O + B₂H₆) will certainly be influenced by the surface of the solid. The extent of these influences are as yet to be clearly established. In another example, the reactions of B₂H₆ + D₂ and B₂H₆ + B₂D₆ are postulated as proceeding *via* a similar intermediate, yet the latter is 300-fold faster than the former and shows none of the effects of added N₂ and CO₂ as well as S/V that the former does. Clearly they are different reactions. Thus any conclusions based on Marcus's interpretation of these reactions must be viewed with a large amount of reserve.

Other examples illustrating the lack of sufficient data to lead to the establishment of any mechanism are the cases of B₂H₆ + C₂H₄, B₂H₆ + H₂O, and the pyrolysis of B₂H₆. In each of these systems the stoichiometry is yet to be established. Also the kinetics postulated for the first and third cases lead to impossible Arrhenius A factors and the hydrolysis reaction shows a 50% increase in rate in a packed vessel.

These facts coupled with some assumptions which we feel are questionable lead us to the conclusion that in the majority of the systems (6 of 7) no conclusion regarding $\Delta H_{\text{diss}}(\text{B}_2\text{H}_6)$ is warranted by the data. Thus the earlier results do not lead to a conclusive standard for comparison. The fact that 5 of the 7 earlier results derived by Bauer do indeed support our value is felt to be fortuitous.

The present rate data can be used to define limits for the bond dissociation energy of B₂H₆ at two different points. The bond dissociation energy of BH₃CO = E₁ - E₂ ≡ D(BH₃CO). From the equilibrium constant data of Burg² D(B₂H₆) = 2D(BH₃CO) - 9.1 kcal. Now we have seen that it is very likely that E₁ ≤ 23.7 kcal. so that if E₂ = 0, D(BH₃CO) ≤ 23.7 kcal. and D(B₂H₆) ≤ 38.3 kcal. This value will be decreased by 2E₂ if E₂ ≠ 0. In order to arrive at the estimate of D(B₂H₆) = 28.4 kcal., one would have to assign E₂ = 4.9 kcal. While this is not an impossible value it does seem an unreasonable value for the acid-base type of interaction involved in the BH₃ + CO association. The similar reaction of CH₃ with CO which forms a much weaker bond has only a 3 kcal. barrier and is in addition electronically forbidden.¹² It should be noted that this assignment of bond energies gives E₃ = 7.1 kcal.

The other point of relation is mechanistic. If BH₃ + BH₃CO is fast compared to BH₃ + BH₃, then the ratio of rates for these two processes is given by

$$\frac{R_{\text{BH}_3}}{R_{\text{BH}_3\text{CO}}} = \frac{k_r(\text{BH}_3)^2}{k_3(\text{BH}_3\text{CO})(\text{BH}_3)} = \frac{k_r(\text{BH}_3)}{k_3(\text{BH}_3\text{CO})} \quad (11)$$

Here k_r is the recombination rate constant for 2BH₃.

If we substitute the steady-state value for (BH₃)

$$R_{\text{BH}_3}/R_{\text{BH}_3\text{CO}} = k_r K_{1,2}/k_3(\text{CO}) \quad (12)$$

$$= k_r K_{1,2}^2/k_{\text{obsd}}(\text{CO}) \quad (13)$$

(10) See discussion of the exact Burg equation.

(11) S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 549 (1958).

(12) H. E. O'Neal and S. W. Benson, *ibid.*, **36**, 2196 (1962).

where k_{obsd} = the experimental quantity $k_3 K_{1,2}$ (eq. 9).

Now let us assume that over the dynamic range of composition the ratio of these two rates is not more than 0.1. This leads to

$$K_{1,2}^2 \leq 0.1 k_{\text{obsd}}(\text{CO})/k_r \quad (14)$$

or in logarithmic form

$$2 \log K_{1,2} \leq -1 + \log(\text{CO}) + \log(k_{\text{obsd}}/k_r) \quad (15)$$

But $2.3RT \log K_{1,2} = -\Delta H_{1,2} + T\Delta S_{1,2}$ and since $2\Delta H_{1,2} = D_{\text{B}_2\text{H}_6} + 9.1$, we find

$$\frac{-D_{\text{B}_2\text{H}_6} - 9.1 + 2T\Delta S_{1,2}}{2.3RT} \leq -1 + \log(\text{CO}) + \log(k_{\text{obsd}}/k_r) \quad (16)$$

or at 300°K. where $2.3RT \sim 1.4$ kcal.

$$\frac{D_{\text{B}_2\text{H}_6} + 9.1 - 2T\Delta S_{1,2}}{1.4} \geq 1 - \log(\text{CO}) - \log(k_{\text{obsd}}/k_r) \quad (17)$$

or substitution of $\Delta S_{1,2} = 24.8$ gibbs/mole (1 mole/l. standard state)

$$D_{\text{B}_2\text{H}_6} \geq 7.2 - 1.4 \log [k_{\text{obsd}}(\text{CO})/k_r]$$

Using $k_r \sim 10^{10}$ l./mole-sec., $\text{CO} \sim 5 \times 10^{-5}$ mole/l., and the $k_{\text{obsd}} = 1.8 \times 10^{-8}$ sec.⁻¹ we find $D_{\text{B}_2\text{H}_6} \geq 35$ kcal.¹³ The only way in which this could be reduced to 28 kcal. is to assume that $k_r \sim 10^6$ l./mole-sec. This is probably too small to be reasonable. A value of 10^8 would be reasonable and this would lead to $D_{\text{B}_2\text{H}_6} \geq 32$ kcal.¹⁴

Appendix

Earlier we stated that there should be severe reservations placed on the conclusiveness of earlier results; here we will show in detail why this must be so. To do this, each equation considered for the establishment of ΔH_{diss} of B₂H₆ (aside from the BH₃CO system) will be examined:

1. **B₂H₆ + C₂H₄.**¹⁵—Bauer finds $\Delta H^\circ < 38.4$ kcal., but criticizes the kinetics. He is completely justified in the latter since the stoichiometry is not established. The kinetics lead to an impossible Arrhenius A factor for the slow step; our conclusion: the data do not justify any conclusion on $D_{\text{B}_2\text{H}_6}$.

2. **B₂H₆ + PH₃.**¹⁶—The reaction mechanism involves a step very similar to our step 4 ($\text{CO} + \text{B}_2\text{H}_6 \rightarrow \text{CO}:\text{BH}_3 + \text{BH}_3$), namely $\text{PH}_3 + \text{B}_2\text{H}_6 \rightarrow \text{PH}_3:\text{BH}_3 + \text{BH}_3$, and this is found to be faster than the mechanism proceeding *via* $\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$; conclusion: $\Delta H^\circ > 30$ kcal. Note that Bauer assumes that the $\text{PH}_3 + \text{BH}_3$ rate is only 2.3×10^6 l./mole-sec. This would be the lowest value ever obtained for an association reaction presumably not involving an activation energy. Higher values would raise ΔH° by 2.8 kcal. for every power of 10 by which the association rate is increased; our conclusion: $\Delta H^\circ > 33$ kcal. It should be noted that since the reaction product is a solid, the question of a heterogeneous reaction and the rate of nucleation add complexities to the reaction.

3. **Decomposition of Me₂O : B₂H₆(s).**¹⁷—Here the observed reaction is the direct decomposition of a solid complex into gaseous products. There is no basis for any conclusion whatsoever regarding the B₂H₆ equilibrium. The rate of the reaction is obviously controlled by the nature of the surface of the crystals.

(13) See ref. 2, from which by similar argument a limit of 41 kcal. is deduced. The equation used is incorrect.

(14) It should be noted that if BH₃ recombination does actually proceed heterogeneously in the BH₃CO system, the contribution to the rate would not be observable unless the heterogeneous rate was at least 3- to 10-fold faster than the homogeneous rate and the latter coincided with values of $k_r = 10^{10}$ l./mole-sec. and $D_{\text{B}_2\text{H}_6} \leq 36$ kcal.

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

(16) H. Brumberger and R. A. Marcus, *J. Chem. Phys.*, **24**, 741 (1956).

(17) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 296 (1938).

Almost any rate of association of BH₃ would be compatible with the data, but in particular there is no way of deciding whether or not it is homogeneous. Despite these limitations Bauer, on the basis of several questionable assumptions, decides $\Delta H^\circ \leq 33.5$ kcal.; our conclusion: no conclusions are justified by the data.

4. **Pyrolysis of B₂H₆.**¹⁸—Here the stoichiometry is not established nor is the homogeneity of $\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$ determinable. Nevertheless, Bauer concludes $\Delta H^\circ < 38$ kcal. The mechanism is quite complicated and involves intermediates postulated for the $\text{B}_2\text{H}_6 + \text{C}_2\text{H}_4$ reaction which lead to impossibly high Arrhenius A factors. The two sources quoted disagree completely on the mechanism and the values of the rate constants; our conclusion: no conclusions are justified by the data.

5. **B₂H₆ + H₂O.**¹⁹—This system is quite complex and the over-all stoichiometry is unknown. Again there is no way of deciding on the homogeneity of $\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$ since it is not the slow step. The rates in this reaction were followed by pressure changes and these are quite small and dependent on the ratios of the reactants. The usual case corresponds to a pressure decrease of 3 mm. for complete reaction and the rates are thus very imprecise. Bauer chose to use the rate of H₂ evolution as a measure of the slow step although it is clear from the paper that most of the H₂ comes from surface reactions whose extent depends on the initial ratio of the reactants. Also note that the rate increases 50% in a packed vessel. Nevertheless it was concluded that $\Delta H^\circ < 30$ kcal.; our conclusion: no conclusions are justified by the data.

6. **B₂H₆ + D₂.**²⁰—Here again $\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$ is not rate determining so no conclusion regarding its homogeneity can be made. It is believed that the rate is surface controlled and this is confirmed by independent work of K. S. Pitzer (unpublished). Marcus' interpretation of the data predicts an order change in B₂H₆ from 1/2 to 3/2 when the rate becomes first order in D₂. This is not observed. The rate remains 3/2 order in B₂H₆ even when the rate is first order in D₂ at low [D₂]. Both N₂ and CO₂ slow the rate, while increasing S/V by tenfold doubles the rate. This is not compatible with Marcus' mechanism. Note that in deriving the mechanism Marcus assumed $R(\text{BH}_3 + \text{D}_2) \gg R(\text{BH}_3 + \text{BH}_3)$. Furthermore, from Marcus' mechanism, $k_7/k_3 = 4$ at 55°, where k_7 is the rate constant for $\text{BH}_3 + \text{D}_2 \rightleftharpoons \text{BH}_2\text{D} + \text{HD}$, and k_3 is for $\text{BH}_3 + \text{B}_2\text{D}_6 \rightleftharpoons \text{BH}_3\text{BD}_3 + \text{BD}_3$ (or any other disproportionation such as $\text{BH}_2\text{DBD}_3 + \text{BHD}_2$). This makes the mechanism the same as that for exchange of B₂H₆ with B₂D₆; however, the latter is 300-fold faster than the former! Marcus noted this but couldn't explain it. This leaves his mechanism very dubious. Because of the zero-order dependence on D₂, no information is forthcoming on k_7 . In Bauer's work an error appears in the assignment of the observed rate constant to $k_7 K_{\text{eq}}^{1/2}$ whereas it should be assigned to $k_3 K_{\text{eq}}^{1/2}$ and then concludes that $\Delta H^\circ < 33$ kcal.; our conclusion: no conclusions are justified by the data.

7. **B₂H₆ + B₂D₆ Exchange.**²⁰—Marcus concludes this and the preceding reaction have the same slow step, thus the two rate constants should be identical. In fact, the self-deuteration is about 300-fold faster and the reaction is not sensitive to S/V or to added N₂ or CO₂. They are clearly different reactions. Here the slow step is $\text{BH}_3 + \text{B}_2\text{D}_6$ and not the $\text{B}_2\text{H}_6 \rightleftharpoons 2\text{BH}_3$ reaction. Consequently, the homogeneity of the latter

(18) (a) R. P. Clarke and R. N. Pease, *ibid.*, **73**, 2132 (1951); (b) J. K. Bragg, L. V. McCarty, and F. J. Norton, *ibid.*, **73**, 2134 (1951).

(19) H. G. Weiss and I. Shapiro, *ibid.*, **75**, 1221 (1953).

(20) (a) P. C. Maybury and W. S. Koski, *J. Chem. Phys.* **21**, 742 (1953); (b) R. A. Marcus, *ibid.*, **23**, 1107 (1955).

is not established. Despite this a value of $\Delta H^\circ < 27$ kcal. is arrived at. Further, the reported activation energy of 21.8 ± 3 kcal. leads to a value of A_3 of $10^{11.3}$ l./mole-sec. This is about 3 powers of 10 too high for a reaction of this type (step 3 refers to $\text{BH}_3 + \text{B}_2\text{D}_6$).

No other A factor comparable to this has ever been obtained for such complex species. The lower limit of E of 18.3 kcal. would reduce this to $10^{9.3}$ l./mole-sec. and be more reasonable. We conclude again that no value can be deduced for ΔH° .

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARLETON COLLEGE, NORTHFIELD, MINN.]

The Thermodynamics of the Thermal Decomposition of Acetic Acid in the Vapor Phase¹

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Acetic acid in the vapor phase has been found to decompose reversibly into ketene, water, and acetic anhydride at temperatures in the range 268–330°. Equilibrium constants for the two simultaneous equilibria implied have been measured over this temperature range, and ΔH° and ΔS° for the two reactions have been obtained. The calculated heats of reaction are in good agreement with calorimetric values. The product of the activity coefficients of water and acetic anhydride in acetic acid solution have also been calculated and found to agree with literature values. On the other hand, the entropy of acetic acid monomer which is derived differs from the spectroscopic value. For this reason, several changes in the statistical thermodynamic treatment are suggested to yield a set of thermodynamic functions for acetic acid monomer which are in fair agreement with all the experimentally determined thermodynamic properties of acetic acid.

More than 30 years ago Muhlhauser and Trautz² reported equilibrium constants for the thermal decomposition of acetic acid vapor, at 400–640°, into the assumed products acetic anhydride and water. The value which they obtained for ΔH for the reaction, 41 kcal., seemed questionable at the time and can now be ruled out altogether when compared with the calorimetric value, 10 kcal.³ Later, in a study of the kinetics of the thermal decomposition of acetic acid vapor at 500–900°, Bamford and Dewar⁴ found that ketene and water are produced in one of several reactions which occur. It is therefore possible that Muhlhauser and Trautz, who did not confirm the identities of the products, were actually studying the latter reaction. In fact, a rough reworking of their data can be made, giving a ΔH of approximately 35 kcal. for the ketene reaction, which is comparable to the calorimetric value of 31 kcal.³ A further study of the equilibria occurring in acetic acid vapor at high temperature thus seems called for.

The possibility that the thermodynamics of the reaction



can be obtained offers a route to the thermodynamic properties of acetic acid monomer, because both ketene and water have been thoroughly studied. The most recent and complete study of acetic acid in the gaseous state is that of Weltner,⁵ whose values for the monomer are based mainly on statistical thermodynamics. At the time of his publication, there were uncertainties regarding (1) the magnitude of the potential barrier hindering the internal rotation of the methyl group, (2) the frequency of the O–H out-of-plane bending motion and perhaps one or two of the other vibrational assignments, and (3) the energy difference between the *cis* and *trans* isomers for rotation of the O–H group about the C–O bond. During the intervening years the barrier to rotation of the methyl group has been determined by microwave spectroscopy,⁶ but doubt remains on the other points. Therefore, it was felt that an independent determination of the entropy of acetic acid monomer would be desirable.

Finally, a comparison between the vapor phase decomposition and the liquid phase decomposition recently reported⁷ should be of interest.

Experimental

Reagents.—Analytical reagent grade acetic acid was purified and its purity checked as described previously.⁷ The mole fraction of water in the acid was about 7×10^{-4} . (The acid used in the experiments at 300.6°, however, had a mole fraction of water of approx. 1.3×10^{-3} .) Reagent grade acetic anhydride was distilled at atmospheric pressure before use as a titrant in the water determinations.

Apparatus for Thermal Decomposition.—A static system was employed. A 2-l. reaction vessel, which was made from 110-mm. Pyrex tubing, was located in an electrically heated, crucible type furnace. Transfer of samples to and from the reaction vessel was accomplished by means of a conventional vacuum system.

At the beginning of an experiment, the reaction vessel was evacuated for 2 hr. at the temperature to be employed for the thermal decomposition. A sample of acetic acid was then admitted by connecting the vessel, through a three-way capillary stopcock and heated tubing, to a reservoir of liquid acetic acid, which was held at a temperature high enough to produce a vapor pressure somewhat greater than the pressure desired in the reaction vessel. The acetic acid vapor was equilibrated anywhere from several hours to several days. In some experiments, indicated in Table I, the initial temperature of the sample was at least 15° higher than the final temperature. This initial heating period was long enough to give an extent of reaction greater than that found ultimately at the final temperature. Equilibrium was thus approached from the product side of the reaction.

For removal of the sample, the three-way stopcock was turned to connect the vessel to a U-trap, filled with glass beads, at –78°, which in turn led to a small flask, at –196°, containing a weighed quantity (3 g.) of water. Unreacted acetic acid, acetic anhydride, and water were retained in the trap at –78°, while ketene passed through and was frozen in the flask at –196°. After a stopcock above this flask was closed, the latter was warmed to room temperature to allow the ketene to react with water to produce acetic acid, which later was determined spectrophotometrically, as described below. The contents of the U-trap were transferred to a small tube, which was sealed from the line and maintained at –78° until the time of analysis.

Temperatures were measured with an iron–constantan thermocouple, calibrated at the melting points of benzoic acid, tin, cadmium, and zinc. The thermocouple was located in a well along the axis of the cylindrical reaction vessel. Thermocouple e.m.f.'s were measured with a Leeds and Northrup potentiometer. The temperature was held constant to within $\pm 1^\circ$ by means of a proportional controller, which supplied current to the main heater around the core of the furnace and to an auxiliary heater in the transite top above the reaction vessel. The temperature variation along the axis of the vessel was found to be no greater than 3° over the upper three-fourths of the vessel. Along the lower one-fourth there was a decrease toward the bottom of about 6°. Perpendicular to the axis of the vessel the variation was 3°. Since the thermocouple was in a position of nearly average temperature, the temperature is believed accurate to $\pm 2^\circ$.

(7) J. A. Knopp, W. S. Linnell, and W. C. Child, Jr., *J. Phys. Chem.*, **66**, 1513 (1962).

(1) Taken in part from the senior honors thesis (1961) of A. J. Hay.

(2) W. Muhlhauser and M. Trautz, *Z. physik. Chem. Bodenstein-Festband*, **319** (1931).

(3) See the Discussion section of this article.

(4) C. H. Bamford and M. J. S. Dewar, *J. Chem. Soc.*, 2877 (1949).

(5) W. Weltner, Jr., *J. Am. Chem. Soc.*, **77**, 3941 (1955). Erratum: *ibid.*, **83**, 5045 (1961).

(6) W. J. Tabor, *J. Chem. Phys.*, **27**, 974 (1957).