

have been calculated for various models of rectangular parallelepipeds by Mittelbach and Porod.<sup>43</sup> In the present study the scattering curve for infinite slit collimation,  $j(s)$ , was calculated for the  $a \times a \times 2a$  case, by decomposing  $i(s)$  into its asymptotic form and the oscillations about this average function.

$$i(x = 2\pi as) = (5\pi/x^4) + u(x) \quad (15)$$

Then

$$\begin{aligned} j(2\pi as) &= 2 \int_0^\infty i(\sqrt{s^2 + t^2}) dt \quad (16) \\ &= \frac{5\pi}{4x^3} + \frac{1}{\pi a} \int_0^\infty u\sqrt{x^2 + y^2} dy \end{aligned}$$

The second term was evaluated by graphical integration.

**Case 3. Two Sphere Model.**—The two spheres touch at a single point. The scattering of such a model, normalized to  $i(0) = 1$ , can be readily calculated for point source collimation

$$i(s) = \frac{1}{2} \left( 1 + \frac{\sin 4\pi rs}{4\pi rs} \right) \phi^2(2\pi rs) \quad (17)$$

where  $\phi^2(2\pi rs)$  is the scattering of a single sphere of radius  $r$ , normalized to  $\phi^2(0) = 1$ . For  $4\pi rs \geq 10$ ,

(43) P. Mittelbach and G. Porod, *Acta Phys. Austriaca*, **14**, 186 (1962).

$\left| \frac{\sin 4\pi rs}{4\pi rs} \right| \leq 0.1$ . Thus, as a first approximation, for large  $4\pi rs$ , we have

$$\bar{i}(s) \simeq \frac{1}{2} \phi^2(2\pi rs) \quad (18)$$

This approximation is still more valid for  $j_n(s) = 2 \int_0^\infty i_n(\sqrt{s^2 + t^2}) dt$ , since the integration of  $i(s)$  smears out the oscillations about its average value. It should be pointed out that for  $r = 17.2 \text{ \AA}$ .,  $4\pi rs \geq 10$  when  $s > 45 \times 10^{-3} \text{ \AA}^{-1}$ . It is this asymptotic behavior of  $j(s)$  which is shown in Fig. 3

$$j(s) = \frac{1}{2} \left( \frac{3}{5} j_0(2\pi rs) \right) = \frac{3}{10} j_0(2\pi rs) \quad (19)$$

where  $j_0(2\pi rs)$  is the scattering of a single sphere (see above).

The function  $j(2\pi rs)$  describes only the asymptotic behavior and as such does not yield for small values of  $s$  the gaussian form corresponding to the experimental radius of gyration,  $R_0$ .

**Acknowledgment.**—We wish to express our appreciation to Professors C. Sadron and H. Benoit for their great interest in and encouragement of this work; furthermore, S. N. Timasheff wishes to thank them also for extending their hospitality and making their facilities available to him during his stay in Strasbourg.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 27, N. Y.]

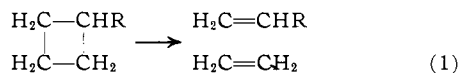
## The Kinetics of the Thermal Decomposition of Methyl Cyclobutanecarboxylate<sup>1</sup>

BY MARIA ZUPAN AND W. D. WALTERS

RECEIVED AUGUST 26, 1963

In the neighborhood of 400°, methyl cyclobutanecarboxylate decomposes in the vapor phase to yield ethylene and methyl acrylate. The reaction is a first-order process which occurs homogeneously and does not seem to be affected significantly by the addition of nitric oxide or propylene. Experiments near 10 mm. at 380–420° indicated that the activation energy for the decomposition is  $57.3 \pm 0.3$  kcal./mole. The first-order rate constant may be expressed as  $k = 7.0 \pm 0.1 \times 10^{14} \exp(-57300/RT)$  sec.<sup>-1</sup>. When the results from the present study are compared with previous data for related cyclobutane derivatives (C<sub>4</sub>H<sub>7</sub>-R), it is found that the rate constants at 390° decrease with a change in the nature of R in the order: HC=O > CH<sub>3</sub>C=O > CH<sub>3</sub>OC=O.

From the results of earlier studies of the homogeneous thermal decompositions of monosubstituted cyclobutanes,<sup>2-5</sup> it is possible to make some comparisons of the effect of a change in the structure of the substituent R upon the kinetics of the first-order process



The decompositions of compounds in which R is an alkyl group do not differ greatly in activation energy ( $E = 61.2$ – $62.6$  kcal./mole).<sup>2,3</sup> On the other hand, when R is HC=O or CH<sub>3</sub>C=O, a significantly lower activation energy (53.3, 54.5 kcal./mole) is observed.<sup>4,5</sup> Although the pre-exponential factor ( $A$ ) is slightly lower also for the carbonyl derivatives, the combined effect of the changes of  $E$  and  $A$  results in a considerably higher rate constant for a compound where R is HC=O or CH<sub>3</sub>C=O compared to that for any monoalkylcyclobutane studied thus far. The faster rate makes it possible to study such compounds in a static system at temperatures of 360–410°. As a result of the considerable influence of substituents containing >C=O,

it was of interest to investigate the decomposition of methyl cyclobutanecarboxylate (where R is CH<sub>3</sub>O-C=O). The decompositions of esters of organic acids at temperatures from 250 to 600° have been studied extensively. Many of the esters with a β-H on the alkoxy group have been observed to decompose into an acid and an olefin.<sup>6</sup> The decompositions of methyl esters take place much less readily,<sup>6</sup> and published studies indicate that the pyrolyses of certain methyl esters may be complicated by free radical chain processes<sup>6b</sup> and heterogeneous effects.<sup>7</sup> In view of the slowness of the thermal decompositions of methyl esters (not containing a cyclobutane ring), it seemed likely that the primary reaction of methyl cyclobutanecarboxylate would be a ring cleavage as shown in eq. 1. In that case the influence of the CH<sub>3</sub>OC=O, CH<sub>3</sub>C=O, and HC=O groups upon the kinetics of the ring cleavage could be compared.

### Experimental

**Materials.**—Methyl cyclobutanecarboxylate was synthesized by means of the reaction of diazomethane with cyclobutanecarboxylic acid. The diazomethane was prepared by the addition of nitrosomethylurea to a cold mixture of 50% aqueous KOH solution and ether. The cyclobutanecarboxylic acid, purchased from the Kaplop Laboratories, was dissolved in ether and added slowly to a stirred ethereal solution of diazomethane.

(6) (a) E. M. Bilger and H. Hibbert, *ibid.*, **58**, 823 (1936); (b) C. D. Hurd and F. H. Blunck, *ibid.*, **60**, 2419 (1938); (c) A. T. Blades, *Can. J. Chem.*, **32**, 366 (1954); (d) A. Maccoll, "Kekulé Symposium on Theoretical Organic Chemistry," Butterworths Scientific Publications, London, 1959, p. 243.

(7) F. W. R. Steacie, *Proc. Roy. Soc. (London)*, **A127**, 314 (1930).

(1) This work was supported by a grant from the National Science Foundation.

(2) S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961); this article gives references to previous studies of alkylcyclobutanes.

(3) M. Zupan and W. D. Walters, *ibid.*, **67**, 1845 (1963).

(4) B. C. Roquette and W. D. Walters, *J. Am. Chem. Soc.*, **84**, 4049 (1962).

(5) L. G. Daignault and W. D. Walters, *ibid.*, **80**, 541 (1958).

After the unreacted acid had been neutralized with a sodium carbonate solution, the ether was volatilized and then the ester was fractionated in a spinning-band column at a reflux ratio of about 15:1. Fractions VII and VIII (before gas chromatographic purification) had boiling points of 134.9–135.4° and 135.4–135.8° at 750.3 mm. and values of  $n_D^{20}$  of 1.4267 and 1.4269, respectively, compared with literature values<sup>8</sup> of 134.5° at 754 mm. and  $n_D^{20}$  1.42596. The infrared spectrum of VII was determined on a 6.7-mm. vapor sample in a 1-m. cell of a Perkin-Elmer Model 21 instrument. Moderate to strong maxima were observed at 3.4–3.5, 5.7, 6.95, 7.4, 8.0, 8.2–8.8, and 9.45  $\mu$  with smaller absorptions at 10.25, 10.95, 12.6, 13.6, and 14.5  $\mu$ . Since gas chromatographic analysis of VII and VIII indicated purities of about 96–97%, the samples were purified further on a Perkin-Elmer 154D gas chromatograph with a 2-m. R-X column (polypropylene glycol on Chromosorb) heated to 110°. The purified samples VIIa and VIIIa after drying over anhydrous calcium sulfate had purities of at least 99.9% as determined by gas chromatography. Sample VIIIa was used in the experiments for which rate constants are given here. Methyl acrylate from Eastman Kodak Co. was dried and degassed before use. Its purity measured gas chromatographically was 99.5%. Other substances were the same as those in a previous study.<sup>3</sup>

**Apparatus and Technique.**—The apparatus employed in this work has been described already.<sup>3</sup> In the present study the packed vessel C (290 ml.) was placed in the same furnace which had been used for unpacked reaction vessel A (359 ml.). The pressure increase was measured to  $\pm 0.01$  mm. on a wide-bore mercury manometer with a 25-mm. Gaertner cathetometer. To prevent condensation of the ester or absorption in the stopcock grease, the capillary tubing, manometer, and stopcock adjacent to the reaction vessel were heated electrically with Nichrome resistance wire and the heated parts were surrounded by asbestos or glass. Since in the preliminary experiments 1 through 8 (not used in the kinetic study) the pressure readings may have been influenced to a very small extent by absorption of the reactant in the Dow-Corning silicone grease on the stopcock, the heating was increased after experiment 8. Tests indicated that no measurable absorption of either the reactant or methyl acrylate occurred under the conditions used for rate studies. As a precautionary measure to keep the surface deactivated, samples of methyl acrylate or the reactant were kept in the reaction vessel for an hour before the start of work on each day.

**Analyses.**—After the decomposition had been allowed to proceed for the desired time, the reaction mixture was removed and separated into three fractions; fraction a contained the material volatile at  $-196^\circ$ ; fraction b substances volatile at  $-119^\circ$  but condensable at  $-196^\circ$ ; fraction c substances condensable at  $-119^\circ$ . Fraction a amounted to only 0.1–0.2% of fraction b and was removed without analysis. Fraction b, when analyzed on a 3-m. Perkin-Elmer D gas chromatographic column (tetraiso-butylene) at room temperature, showed the same retention time as pure ethylene. No other components could be detected and the chromatograms gave evidence that ethylene constituted at least 99.9% of fraction b. The mass spectrum of this fraction agreed well with the mass spectrum of ethylene on the same Consolidated 21-620 instrument. Vapor phase chromatograms of fraction c obtained with a 2-m. R-X column at 112° showed only two components, having retention times (4.25 and 19.5 min.) identical with those for methyl acrylate and methyl cyclobutanecarboxylate, respectively. It is estimated that no other component in amount greater than 0.1–0.2% could have been present. Component "4.25" was trapped out and analyzed mass spectrometrically. For the region measured ( $m/e$  12 to 86) the mass spectrum agreed well with that for methyl acrylate. Illustrative of the agreement are the following data for peaks greater than 8.5% of the highest peak (where the masses are given and then the observed ion intensities for component "4.25" and methyl acrylate): 15 (34.80, 35.07), 26 (15.33, 15.46), 27 (70.96, 70.80), 55 (100, 100), 85 (8.60, 8.72). Thus, the products are in accord with a ring cleavage of the type shown in eq. 1 where R is  $\text{CH}_3\text{OC}=\text{O}$ . Over the extent of decomposition investigated in this work this seems to be the only reaction of significance. Methyl acrylate (4 mm., 410°) gave no detectable pressure change in 25 min.

On the basis of the occurrence of reaction 1 in a system of constant volume the pressure increase  $\Delta P$  (observed pressure change corrected for dead space) should equal the pressure of ethylene formed. The experimental observations which are shown in Table I indicate that such a relationship exists under the conditions used in this study. The pressure of ethylene ( $P_E$ ) at the reaction temperature was calculated from the measured amount of fraction b. For the seven experiments without added gas in the unpacked reaction vessel the average value of the ratio  $P_E/\Delta P$  was  $0.99 \pm 0.01$ . Therefore, the use of pressure readings for measuring the extent of reaction seemed warranted. From the data obtained in the last two experiments shown in Table I there does not appear to be a significant change in the

TABLE I  
PRESSURE INCREASE COMPARED WITH THE PRESSURE OF ETHYLENE FORMED DURING THE PYROLYSIS OF METHYL CYCLOBUTANECARBOXYLATE

Temp., °C.	Exptl. cond. <sup>a</sup>	$P_0$ , mm.	$\Delta P$ , mm. <sup>c</sup>	$P_E$ , mm.
390	A	6.47	2.04	1.97
390	A	9.85	3.68	3.63
400	A	9.00	3.28	3.23
410	A	9.29	3.44	3.43
420	A	10.07	3.42	3.47
419	A	10.33	3.58	3.58
420	A	10.56	3.81	3.81
410	A, 0.77 mm. NO	9.16	3.39	3.21
410	C	11.45	4.56	4.34

<sup>a</sup> A denotes unpacked vessel and C denotes packed vessel with  $27 \times$  the  $S/V$ . <sup>b</sup> Initial pressure of methyl cyclobutanecarboxylate. <sup>c</sup> All pressures in this study are in terms of mercury at 0°

course of the reaction in the presence of nitric oxide or in a packed vessel.

## Results

**Order and Homogeneity of the Reaction.**—In Table II are shown the first-order rate constants calculated from the quarter-times observed under various conditions. The value of the rate constant at 410° was not altered by a doubling of the initial pressure. Likewise, linear behavior was observed for plots of  $\log [P_0/(P_0 - \Delta P)]$  vs. time over the portion of the decomposition studied (0 to 36%). In nineteen experiments in the unpacked reaction vessel over the temperature range 380–420° with initial pressures of 6–12 mm. the average value of  $t_{1/4}/t_{1/8}$  was  $2.12 \pm 0.03$  which is in reasonable agreement with the value of 2.15 expected for a first-order reaction.

TABLE II  
FIRST-ORDER RATE CONSTANTS FOR THE DECOMPOSITION OF METHYL CYCLOBUTANECARBOXYLATE UNDER VARIOUS CONDITIONS

Temp., °C.	$P_0$ , mm.	$10^4 k$ , sec. <sup>-1</sup>	Added gas, <sup>a</sup> mm.
410.0	6.30	3.35	
409.8	9.29	3.25	
410.0	9.70	3.24	
409.9	9.92	3.20	
409.8	10.57	3.17	
410.0	11.86	3.33	
409.9	9.75	3.30	3.18, C <sub>3</sub> H <sub>6</sub>
409.9	11.06	3.33	4.08, C <sub>3</sub> H <sub>6</sub>
410.0	9.71	3.40	2.51, NO
409.9	9.16	3.28	0.77, NO
			Packed vessel, C
410.1	10.45	3.46	
410.1	11.45	3.50	
410.1	12.01	3.49	

<sup>a</sup> C<sub>3</sub>H<sub>6</sub> means propylene.

In the packed vessel ( $S/V$  increased  $27 \times$ ) the rate constants averaged about 7% higher than those in the unpacked vessel. The rate constants in the experiments with added propylene or nitric oxide were essentially the same (averaging only 2–4% higher) as the constants for pure methyl cyclobutanecarboxylate under similar circumstances. Thus there is no evidence for the occurrence of free radical chain processes or heterogeneous reactions under the conditions used for experiments in the unpacked bulb.

**Activation Energy.**—The influence of temperature upon the rate of decomposition of methyl cyclobutanecarboxylate was investigated at 10° intervals from 380 to 420° with initial pressures of 8.7–10.8 mm. All

(8) G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1804 (1948).

of these experiments were performed in the unpacked vessel with the experimental factors, except temperature, kept nearly the same for each decomposition. The Arrhenius plot of  $\log k$  vs.  $1/T$  for the fifteen experiments is shown in Fig. 1. The slope of the best straight line drawn by inspection through the experimental points indicated an activation energy of 57.2 kcal./mole and a least squares analysis of the data with an IBM 650 computer gave an activation energy of  $57.3 \pm 0.3$  kcal./mole. With 57.3 for  $E$ , a value of  $A$  was calculated for each experiment from the expression  $k = A \exp(-E/RT)$ . With the mean of  $A$  and its average deviation the first-order rate constant can be expressed as  $k = 6.95 \pm 0.09 \times 10^{14} \exp(-57,300/RT)$  sec.<sup>-1</sup>.

### Discussion

The findings of the present study indicate that the initial decomposition of methyl cyclobutanecarboxylate at 380–420° yields ethylene and methyl acrylate by a first-order reaction. The mode of decomposition seems to be in accord with that observed for other monosubstituted cyclobutanes and does not resemble the previously studied decompositions of methyl esters of other organic acids. Under the present conditions the primary decomposition of the cyclobutane ester does not involve free radical chain processes or heterogeneous effects which have been reported earlier for certain methyl esters. The absence of a suitable type of alkyl group precludes olefin formation from the alkoxy portion of the molecule, but ethylene formation occurs as a result of ring cleavage in the acid portion of the compound more rapidly than any alternative mechanism, e.g., breaking of a single bond associated with the  $\text{CH}_3\text{O}-\text{C}=\text{O}$  substituent and subsequent chain-propagating steps.

The kinetics of the pyrolysis of methyl cyclobutanecarboxylate may be compared with those of other cyclobutane derivatives. In the present instance the experimental frequency factor ( $6.95 \times 10^{14}$  sec.<sup>-1</sup>) has been used to evaluate the entropy of activation at 390° from the relationship  $A = \kappa e(k_B T/h) \exp(\Delta S^\ddagger/R)$ . The value of +5.8 e.u. obtained for  $\Delta S^\ddagger$  is shown in Table III together with the entropies of activation of various cyclobutanes. Likewise the values of the kinetic parameters ( $A$  and  $E$ ) and the rate constants at 390° are given in Table III.

TABLE III  
COMPARISON OF THE DECOMPOSITIONS OF CYCLOBUTANE DERIVATIVES ( $\text{C}_4\text{H}_7\text{-R}$ )

R	$10^{-14}A$ , sec. <sup>-1</sup>	$\Delta S^\ddagger$ , <sup>a</sup> e.u. at 390°	$E_{\text{act}}$ , kcal. mole	$10^4 k$ , <sup>b</sup> sec. <sup>-1</sup> at 390°	Ref.
HC=O	2.7	3.9	53.3	7.4	4
CH <sub>3</sub> C=O	3.4	4.4	54.5	3.7	5
CH <sub>3</sub> O-C=O	6.95	5.8	57.3	0.91	c
H	42	9.4	62.5	.106	9
<i>i</i> -C <sub>3</sub> H <sub>7</sub>	43.1	9.4	62.6	.101	3
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	34	9.0	61.6	.17	2

<sup>a</sup> Values calculated from pre-exponential factor ( $A$ ) with  $\kappa = 1$ . <sup>b</sup> Values computed from the rate expressions given in the references cited. <sup>c</sup> Present study.

From the data in Table III it is evident that each of the substituents containing  $>\text{C}=\text{O}$  has a more marked effect on the rate of decomposition than an alkyl substituent. The ester, ketone, and aldehyde have lower energies of activation and lower frequency factors (likewise smaller entropies of activation) than cyclobutane or a monoalkylcyclobutane. The differences should be related to the changes in the molecular structure of the substituents, and to explain the lowering of

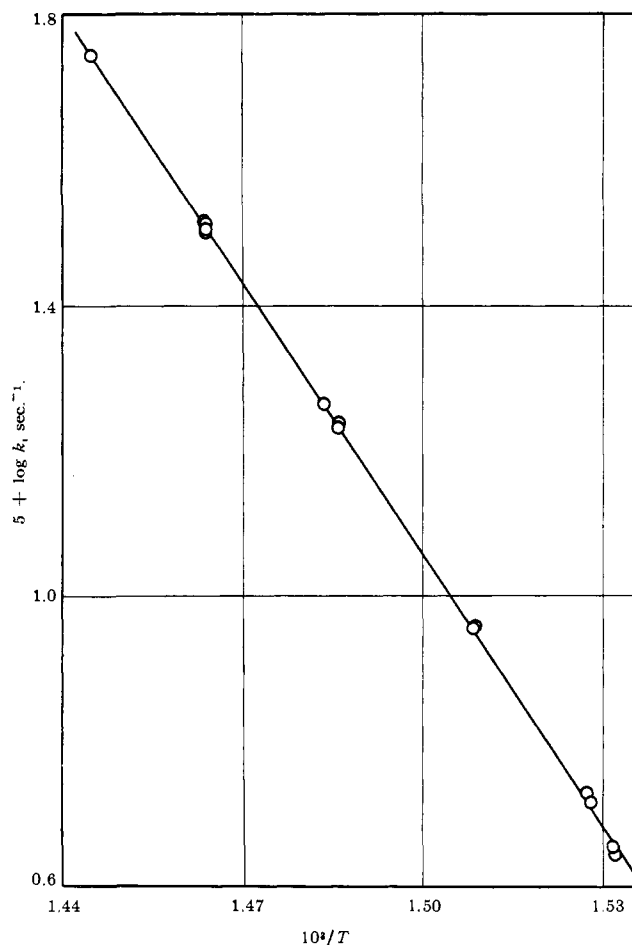


Fig. 1.—First-order rate constants for the decomposition of methyl cyclobutanecarboxylate at various temperatures; initial pressure,  $\sim 10$  mm.

activation energy, it has been suggested that if a biradical is involved in the ring cleavage process, the biradical formed from cyclobutane carbonyl derivatives would be expected to possess more resonance energy than a biradical formed from an alkylcyclobutane.<sup>4,5,10</sup> A greater resonance energy for the biradical might result in a lower energy for the activated complex leading to the biradical. If the carbonyl substituent lowers the energy of the activated complex more than the energy of the reactant, the decrease in the activation energy observed for carbonyl derivatives could be accounted for. Resonance may affect the entropy of the biradical and thus the entropy of activation. With a biradical intermediate the over-all rate of formation of molecular products will be dependent also upon the relative rates of decomposition and recyclization of the biradical<sup>11</sup> and the precise effect of substituents upon these rates for the biradicals is not known.

If the decomposition occurred by way of a ring cleavage directly into  $\text{CH}_2=\text{CH}_2$  and  $\text{CH}_2=\text{CHR}$  without the formation of a biradical, a lower activation energy might be due in part to the effect of resonance stabilization of the decomposition products upon the energy of the activated complex. For monosubstituted cyclobutanes where R is  $\text{HC}=\text{O}$ ,  $\text{CH}_3\text{C}=\text{O}$ , or  $\text{CH}_3\text{OC}=\text{O}$  the main product of decomposition besides ethylene is

(9) R. W. Carr, Jr., and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963).

(10) P. Nangia and S. W. Benson, *J. Am. Chem. Soc.*, **84**, 3411 (1962). That resonance could stabilize a radical of the type  $\text{CH}_2\text{CH}=\text{O}$ , which would have a contributing structure  $\text{CH}_2=\text{CHO}$ , was suggested by F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935, p. 113.

(11) S. W. Benson and P. S. Nangia, *J. Chem. Phys.*, **38**, 18 (1963).

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 Taft<sup>12</sup> 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.<sup>13</sup> They found that this conclusion was in accord with molecular orbital calculations. In  $\alpha,\beta$ -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.<sup>14</sup>

(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 463.

Ingold<sup>15</sup> 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.

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## The Kinetics of the Decomposition of $BH_3CO$ and the Bond Dissociation Energy of $B_2H_6$ <sup>1</sup>

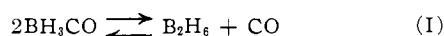
BY MICHAEL E. GARABEDIAN AND SIDNEY W. BENSON

RECEIVED NOVEMBER 17, 1962

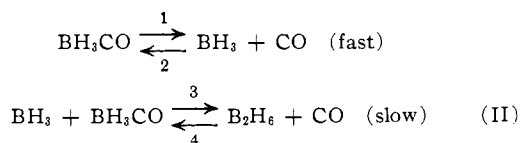
A reanalysis of the kinetic data on  $BH_3CO$  decomposition to give  $1/2 B_2H_6 + CO$  is shown to be in excellent agreement with the original mechanism, II in text. By integration of the exact, steady-state rate law and fitting to the data it is shown that  $k_3/k_2 < 10^{-3}$  so that the assumption 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,  $A_3 = 10^{8.16}$  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

Burg<sup>2</sup> 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,<sup>3</sup> 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 spectrophotometrically<sup>4</sup> 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.<sup>5</sup>

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.

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(2) A. B. Burg, *J. Am. Chem. Soc.*, **74**, 3482 (1952); **69**, 780 (1937).

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

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