

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 30, NUMBER 3

MARCH, 1959

Kinetics of the Thermal Decomposition of Dimethylmercury. I. Cyclopentane Inhibition

MORLEY E. RUSSELL AND RICHARD B. BERNSTEIN

Chemistry Department, University of Michigan, Ann Arbor, Michigan

(Received July 17, 1958)

The kinetics of the pyrolysis of gaseous dimethylmercury have been studied in the presence and absence of cyclopentane inhibitor from 290–375°C for the inhibited and 265–350°C for the uninhibited reactions. The decomposition in excess cyclopentane is first order, with methane the major product (accounting for >95% of the carbon). Rate constants are dependent upon the ratio of dimethylmercury (DMM) to cyclopentane and upon total pressure. The constant for DMM loss is: $k_D = 1.1 \times 10^{15} \exp(-55\,900/RT) \text{ sec}^{-1}$. The rate constant (from combined data on DMM loss and CH₄ formation) extrapolated to the fully inhibited, high-pressure limit is: $k_1 = 5.0 \times 10^{15} \exp(-57\,900/RT) \text{ sec}^{-1}$.

The data for the uninhibited decomposition agree with the literature; a partial mechanism is suggested which predicts the transition from chain to nonchain behavior with increasing temperature.

For the inhibited reaction the following mechanism is proposed: (1) $\text{Hg}(\text{CH}_3)_2 \rightarrow \text{HgCH}_3 + \text{CH}_3$, (2) $\text{HgCH}_3 \rightarrow \text{Hg} + \text{CH}_3$, (3) $\text{CH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{CH}_4 + \text{CH}_3\text{HgCH}_2$, (4) $\text{CH}_3 + \text{C}_5\text{H}_{10} \rightarrow \text{CH}_4 + \text{C}_5\text{H}_9$, (5) $\text{CH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{C}_2\text{H}_6 + \text{HgCH}_3$, (6) $2 \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$, (7) $\text{CH}_3\text{HgCH}_2 \rightarrow \text{HgCH}_3 + \text{CH}_2$.

Using the present value of $E_1 = 57.9 \pm 1.4 \text{ kcal/mole}$ in conjunction with known thermochemical data, $E_2 = 0 \pm 3 \text{ kcal/mole}$. From the inhibition data, $k_3/k_4 = 0.7 \pm 0.2$ at 300°C, with a very small temperature coefficient. The inert gas pressure effect is evidence for the unimolecular nature of step (1).

INTRODUCTION

PREVIOUS work on the pyrolysis of dimethylmercury has been reviewed by Long¹ and Srinivasan.² The present paper (I) reports new experimental data on the kinetics of the decomposition carried out in the presence and absence of cyclopentane inhibitor and inert gases. The results indicate that short methyl radical chains are involved in the (uninhibited) decomposition and that the activation energy for the initial unimolecular Hg—C bond rupture step (in the high-pressure limit) is significantly higher than previously supposed, yielding a value close to zero for the dissociation energy of the second Hg—C bond. The subsequent paper (II) deals with the C¹³ kinetic isotope effect in the decomposition and its relation to the over-all kinetics.

EXPERIMENTAL³

A conventional high-vacuum apparatus (static system) was used. The surface of the Pyrex reaction

vessel (volume 187 ml) was conditioned to a reproducible state² by performing a large number of preliminary decompositions before making kinetic measurements.

The dimethylmercury (DMM) was prepared by the method of Gilman and Brown,⁴ fractionated in a distillation column, dried with P₂O₅, distilled *in vacuo*, and stored in the dark at -78°C. Physical properties were as follows: vapor pressure (mm Hg), 17.2 (0°C), 49.6 (20°C); boiling range 92–93°C (740 mm Hg); freezing point, -40.5°C; molecular weight (by vapor density), 229 (calc 230.7); %C, 10.5 (calc 10.41); %Hg, 86.4 (calc 86.96). The infrared spectrum of the vapor agreed with the literature.⁵ The proton magnetic resonance spectrum of the liquid consisted of a peak with a shift of -3.90 ppm relative to H₂O (cf. the usual value of -4.0 ppm for the CH₃ group in aliphatic compounds) and two weak symmetrical satellites. The classical collision diameter of the vapor (as measured by Dr. G. A. Miller in this laboratory using the radiometer technique) was found to be $7.1 \pm 0.1 \text{ \AA}$ at 25°C.

Cyclopentane (Phillips Company) was purified by

¹ L. H. Long, *Trans. Faraday Soc.* **51**, 673 (1955).

² R. Srinivasan, *J. Chem. Phys.* **28**, 895 (1958).

³ For further details, see Ph.D. dissertation, M. E. Russell, University of Michigan (1958), available from University Microfilms, Ann Arbor, Michigan.

⁴ H. Gilman and R. E. Brown, *J. Am. Chem. Soc.* **52**, 3314 (1930).

⁵ H. S. Gutowsky, *J. Chem. Phys.* **17**, 128 (1949).

TABLE I. Analysis of products (mole %).

$T(^{\circ}\text{K})$	P_0							
	(mm Hg)	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8^a	$\text{C}_4\text{H}_{10}^a$
603.7	63.4	79.9	4.9	11.5	0.6	2.7	0.1	0.3
620.7	59.7	76.7	3.2	15.4	0.5	3.8	0.1	0.3

^a Combined isomers.

repeated treatments with H_2SO_4 , thorough washing with water, fractionation in a distillation column, and distillation *in vacuo*. The boiling point was 49.5°C (760 mm Hg); $n_D^{25} = 1.4040$.

For experiments on the decomposition of DMM alone, the procedure was as follows: DMM was metered into the thermostated reaction vessel and allowed to decompose for times ranging from 10 min to 145 hr. The contents of the reactor were passed into a trap at -196°C and the product (essentially pure methane with $<2\%$ hydrogen) volatile at this temperature was transferred with a Toepler pump into a measuring volume. The methane was oxidized to CO_2 by cycling through a CuO tube (850°C , then 300°C), removing the H_2O in a trap at -78°C . The quantity of CO_2 was measured (it generally agreed within 1% with that of the CH_4); the CO_2 was then transferred to a sample tube for subsequent mass spectrometer assay ($\text{C}^{13}/\text{C}^{12}$ ratio). The products volatile at -127°C were removed and analyzed mass spectrometrically, or oxidized to CO_2 and/or discarded. The residual material (whose infrared spectrum was identical to that of the DMM) was allowed to warm up, distilled into a weighing tube, and weighed as DMM to give the percent unreacted.

For experiments on the decomposition of DMM in the presence of cyclopentane, the procedure was as follows: DMM and C_5H_{10} were successively metered into the thermostated reactor. After times ranging from 18 min to 190 hr the fraction volatile at -196°C (consisting of CH_4 plus 5–10% H_2) was oxidized as above. The residue⁶ was distilled into a seal-off bulb (*ca* 250 ml) and pyrolyzed for 24 hr at 450°C (sufficient to decompose $>99.9\%$ of the DMM). The mercury was dissolved in hot, concentrated HNO_3 and titrated with KNCS to give the percent DMM unreacted. For experiments of short duration (10 min and greater, $T > 325^{\circ}\text{C}$), DMM was thoroughly premixed with C_5H_{10} and stored in a bulb. The mixture was transferred into the reactor with a Toepler pump; subsequent operations were as before. The ratio of DMM to C_5H_{10} in the original mixture was determined by following the same mercury assay procedure.

For certain experiments the total pressure was increased by additions of known amounts of CO_2 (purity

⁶ The very small fraction of this residue volatile at -127°C was analyzed mass spectrometrically and found to contain compounds similar to those in a comparable fraction from a decomposition in the absence of cyclopentane.

$>99.9\%$) or SF_6 (purity $>99\%$) after the DMM (and C_5H_{10}) had been introduced into the reactor.

Carbon in the DMM was quantitatively ($\pm 1\%$) converted to CO_2 by oxidation⁷ of a weighed amount in a Vycor break-seal tube containing CuO and Cu at 850°C for 30 hr. The H_2O was removed at -78°C , the CO_2 measured and stored in a sample tube.

Hydrocarbon analyses were carried out with a Consolidated Model 21-103 mass spectrometer; for certain analyses and separations gas chromatography was utilized.

RESULTS

A. Decomposition of DMM Alone

Table I gives the composition of the hydrocarbon product gases for two typical experiments carried out to about 7% decomposition. The CH_4 , C_2H_4 , and C_2H_6 yields are similar to those of Laurie and Long⁸; the C_3 and C_4 components were not reported previously. The increase in % C_2H_6 with temperature is in accord with the observations of others. As noted by Srinivasan,² the carbon in the products accounted for *ca* 60% of the carbon in the DMM decomposed, with the remainder depositing on the reactor walls.

Laurie and Long⁸ reported first-order kinetics over the range 294 – 333°C ; in the present investigation of the uninhibited reaction no attempt was made to verify the order. Apparent first-order rate constants for dimethylmercury loss [$k_D = (-2.303/t) \log(1-f)$ sec^{-1}] were obtained from measurement of the percent DMM unreacted for experiments carried out under the following conditions: initial pressure of DMM, P_0 , 57.1–76.2 mm Hg; temperature, T , 539.1–623.2°K; fraction decomposed, f , 0.11–0.25. Apparent first-order rate constants for methane formation were calculated,

$$\left(k_M = \frac{1}{(\text{DMM})} \frac{d(\text{CH}_4)}{dt} \right) \\ \cong (\text{CH}_4) / \left[(\text{DMM})_0 \left(1 - \frac{f}{2} \right) t \right] \text{sec}^{-1},$$

for experiments made under the following conditions: P_0 , 59.7–71.8 mm Hg; T , 555.3–620.7°K; f , 0.052–0.095. Least-squares treatment gave the following Arrhenius equations for the uninhibited reaction:

$$k_D = 5.0 \times 10^{13} \exp(-49\,900/RT) \text{sec}^{-1},$$

$$k_M = 3.7 \times 10^{11} \exp(-44\,700/RT) \text{sec}^{-1}.$$

The values for k_D agree well with the data of reference 8 obtained under similar conditions; the present rate constants are 5–20% lower than those of reference 8 (where decompositions were carried out in freshly cleaned Pyrex vessels). Insufficient previous methane

⁷ K. E. Wilzbach and W. Y. Sykes, *Science* **120**, 494 (1954).

⁸ C. M. Laurie and L. H. Long, *Trans. Faraday Soc.* **51**, 665 (1955).

TABLE II. Carbon balance for the inhibited reaction.

T ($^{\circ}\text{K}$)	P_{0t} ^a (mm Hg)	Q	f	% C recovery ^b
576.4	238	0.19	0.11	95
578.0	364	0.25	0.19	96
648.5	323	0.051	1.00	98

^a Total initial pressure ($\text{DMM}_0 + \text{C}_5\text{H}_{10}$).

^b Based on CH_4 plus $\frac{1}{2}$ of the C_2H_6 recovered in products (see footnote 9).

rate data are available for comparison with present k_M values.

B. Decomposition of DMM with Cyclopentane

The decomposition reaction of DMM was considerably less complex when carried out in the presence of excess C_5H_{10} inhibitor. Methane accounted for $>95\%$ of the carbon in the DMM decomposed when the ratio $(\text{DMM})_0/(\text{C}_5\text{H}_{10})$, given the symbol Q , was less than 1. The ratio $\text{C}_2\text{H}_6/\text{CH}_4$ in the products⁹ ranged from 0.02–0.04. Table II lists typical results on the carbon balance for the inhibited reaction; included is one decomposition carried out to completion.

The reaction followed first-order kinetics; no trend in the first-order rate constant (k_D) with extent of reaction was observed. The effect of pressure on k_D at constant Q (0.21) is shown in Table III. The dependence of k_D upon pressure is normal for the unimolecular decomposition of a molecule of the complexity of DMM; this will be discussed later.

First-order rate constants for DMM loss, k_D , were obtained from experiments carried out under the following conditions (P_{0t} is the initial total pressure):

$$P_{0t}, 183\text{--}364 \text{ mm Hg};$$

$$T, 561.7\text{--}649.4^{\circ}\text{K};$$

$$Q, 0.065\text{--}0.25;$$

$$f, 0.10\text{--}0.41.$$

TABLE III. Dependence of k_D on pressure.

T ($^{\circ}\text{K}$)	P_{0t} (mm Hg)	f^a	f_M^b	$k_D \times 10^5$ (sec^{-1})
633.1	321	0.41	0.42	5.60
633.0	157	0.38	0.39	5.05
633.0	94.4	0.36	0.38	4.83
633.2	53.0	0.37	0.36	4.73

^a f = fraction of DMM decomposed in a fixed reaction time (159. \pm 0.5 min).

^b f_M = fraction decomposed based on methane yield (cf. f values based on DMM loss).

⁹ Tracer experiments, described elsewhere,³ showed that approximately one-half of this ethane was derived from the cyclopentane carbon atoms and was therefore spurious, so that the proper ratio lies in the range 0.01–0.02. It was also shown by the tracer technique that $<2\%$ of the carbon in the methane product originated from the cyclopentane, with $>98\%$ derived from the DMM decomposed.

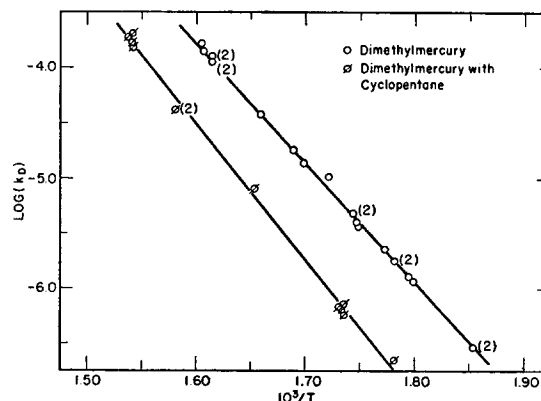


FIG. 1. Arrhenius plot of dimethylmercury rate data.

Similarly, rate constants for methane formation, k_M , were determined from experiments made under the following conditions:

$$P_{0t}, 232\text{--}363 \text{ mm Hg};$$

$$T, 563.2\text{--}648.8^{\circ}\text{K};$$

$$Q, 0.088\text{--}0.31;$$

$$f, 0.042\text{--}0.099.$$

Least-squares analysis of the results gave the following Arrhenius equations for the inhibited decomposition:

$$k_D = 1.1 \times 10^{15} \exp(-55\,900/RT) \text{ sec}^{-1},$$

$$k_M = 3.1 \times 10^{16} \exp(-59\,200/RT) \text{ sec}^{-1}.$$

These results compared with those for the uninhibited decomposition are shown in Figs. 1 and 2.

At any given temperature the two principal variables affecting the rate constants were the ratio Q and the total pressure. Figure 3 shows the dependence of k_M upon Q at 576.6°K in the region of high inhibition (excess C_5H_{10}). Figure 4 presents the dependence of k_M upon total pressure at 632.0°K . For those experi-

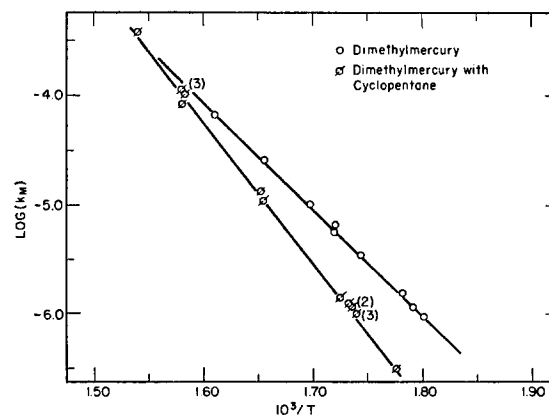


FIG. 2. Arrhenius plot of methane rate data.

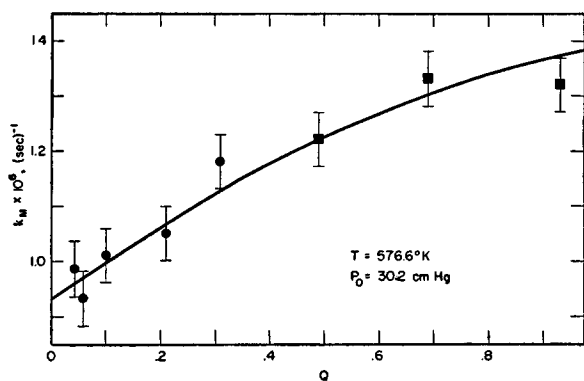


FIG. 3. Dependence of k_M on Q . (Circles corrected to mean temperature, squares corrected to mean temperature and mean pressure.)

ments in which CO_2 (or SF_6) was added, the pressure of DMM plus cyclopentane was *ca* 85–100 mm Hg. From a plot of reciprocal k vs reciprocal pressure only a short extrapolation is required to estimate the high-pressure limit of the (unimolecular) rate constant. The values (and pressure dependence) of k_D (Table III) are consistent with the data of Fig. 4. It may readily be shown (see Discussion) that in the limit of $Q=0$, $k_D = k_M/2 = k_1$, where k_1 is the rate constant for the initial Hg—C bond rupture in DMM. From the intercept of plots such as Fig. 3, k_1 may be obtained. The high-pressure limit of k_1 is determined by a similar procedure with Fig. 4 by noting the percent change in k_M with $1/P_{0t}$. Similarly, values of the high-pressure limit of k_1 are calculated from k_D data.

Figure 5 shows the temperature dependence of the fully corrected k_1 values so obtained,¹⁰ which may be represented by the following least-squares Arrhenius equation:

$$k_1 = 5.0 \times 10^{15} \exp(-57\,900/RT) \text{ sec}^{-1}.$$

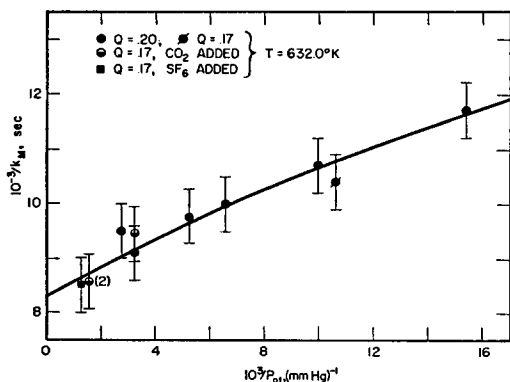


FIG. 4. Dependence of k_M on total pressure.

¹⁰ Comparing values for k_D and $k_M/2$ with k_1 shows only small differences, due to the fact that the corrections for finite Q and $1/P_{0t}$ are of opposite sign and similar magnitudes. Using no corrections, one obtains nearly the same equation: $k_1 = 4.5 \times 10^{15} \exp(-57\,700/RT)$.

The uncertainty (95% confidence interval) in E_1 (the energy of activation) is ± 1.4 kcal/mole; in $\log_{10} A_1$ it is ± 0.52 .

DISCUSSION OF RESULTS

A. Kinetics of the Cyclopentane-Inhibited Decomposition

The following mechanism for the pyrolysis of DMM in the presence of excess C_5H_{10} is proposed. A detailed discussion as to the evidence (both from the literature

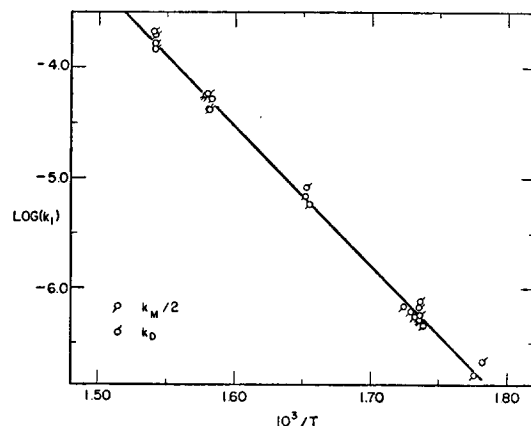


FIG. 5. Arrhenius plot of high-pressure, completely inhibited dimethylmercury rate constants.

and the present work) for each of the individual steps is presented elsewhere.³

- $\text{Hg}(\text{CH}_3)_2 \rightarrow \text{HgCH}_3 + \text{CH}_3$,
- $\text{HgCH}_3 \rightarrow \text{Hg} + \text{CH}_3$,
- $\text{CH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{CH}_4 + \text{CH}_3\text{HgCH}_2$,
- $\text{CH}_3 + \text{C}_5\text{H}_{10} \rightarrow \text{CH}_4 + \text{C}_5\text{H}_9$,
- $\text{CH}_3 + \text{Hg}(\text{CH}_3)_2 \rightarrow \text{C}_2\text{H}_6 + \text{HgCH}_3$,
- $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$,
- $\text{CH}_3\text{HgCH}_2 \rightarrow \text{HgCH}_3 + \text{CH}_2$,
- $\text{CH}_2 + \text{C}_5\text{H}_{10} \rightarrow \text{C}_6\text{H}_{12}$,
- $\text{C}_5\text{H}_9 \rightarrow \text{products}$.

Steady-state solution of the mechanism yields the following equations:

$$(\text{CH}_3) = \frac{k_4(\text{C}_5\text{H}_{10})}{4k_6} \left[\left(1 + \frac{16k_1k_6Q}{k_4^2(\text{C}_5\text{H}_{10})} \right)^{1/2} - 1 \right] \cong \frac{2k_1Q}{k_4}, \quad (1)$$

$$-\frac{d(\text{DMM})}{dt} = k_1(\text{DMM}) [1 + 2Q(k_3 + k_6)/k_4], \quad (2)$$

$$\frac{d(\text{CH}_4)}{dt} = 2k_1(\text{DMM}) (1 + Qk_3/k_4), \quad (3)$$

$$\frac{d(\text{C}_2\text{H}_6)}{dt} = \frac{2k_1Q^2}{k_4} [k_6(\text{C}_5\text{H}_{10}) + 2k_1k_6/k_4]. \quad (4)$$

For the completely inhibited reaction ($Q=0$), $k_1 = k_D = k_M/2$ and $d(C_2H_6)/dt=0$ as expected. With increasing Q , $k_D \equiv -[d(DMM)/dt]/(DMM)$ should increase linearly with Q . Similarly,

$$k_M \equiv [d(CH_4)/dt]/(DMM)$$

should increase linearly¹¹ with Q .

Using a cycle involving the data of McNesby and Gordon¹² and Oswin *et al.*,¹³ one can estimate a value of k_3/k_4 of 0.2 (range 0.05–0.7) at 300°C, with $E_3 - E_4 = 1.2 \pm 1.5$ kcal/mole. From the initial slope of Fig. 3, using Eq. (3), one obtains an experimental value of $k_3/k_4 = 0.7 \pm 0.2$ at 303°C. An estimate of the value of $E_3 - E_4$ was made from the present inhibition data; it is zero within ± 1 kcal/mole.

The thermochemical value for the sum of the dissociation energies of the two Hg—C bonds in DMM is 57.1 ± 2 kcal/mole¹⁴ (or 57.3 ± 4 kcal/mole¹⁵). The present value for the activation energy of Step 1 is $E_1 = 57.9 \pm 1.4$ kcal/mole; assuming a negligible value for E_{-1} , the value for E_2 becomes zero (with an uncertainty of about ± 3 kcal/mole) compared to the previously accepted value^{2,3} of 6 kcal/mole. Pritchard¹⁶ has discussed the interpretation of mercury dialkyl pyrolyses and has suggested that the data for a number of these reactions are consistent with a primary fission into three fragments rather than two. In the particular case of DMM (where previous values of the activation energy were *ca* 51 kcal/mole) he assumed that the decomposition occurs by a combination of this process ("Mode 2") and the more conventional single Hg—C rupture ("Mode 1"). Applying Kassel's theory he estimated the rate constant for decomposition of DMM by Mode 2 to be: $k = 1.9 \times 10^{14} \exp(-55700/RT)$. In view of the present results it is possible that the decomposition may proceed predominantly by Mode 2. In any case the low value of E_2 suggests that the HgCH₃ radical is even less stable than previously supposed.

B. Kinetics of the Uninhibited Decomposition

No completely satisfactory mechanism for the uninhibited pyrolysis of DMM has been developed. The one below is similar to that of Gowenlock *et al.*¹⁷ and Srinivasan² (with minor extensions); it is not fully adequate to explain all the observations.

The first six steps of this mechanism are identical

¹¹ If one includes the next approximation in the series expansion of the term involving the square root in Eq. (1), one obtains the result, $k_M = 2k_1(1 + Qk_3/k_4) [1 - 4k_1k_6Q/k_4^2(C_5H_{10})]$, which explains the negative curvature of the k_M vs Q curve (Fig. 3).

¹² J. R. McNesby and A. S. Gordon, *J. Am. Chem. Soc.* **79**, 825 (1957).

¹³ Oswin, Rebbert, and Steacie, *Can. J. Chem.* **33**, 472 (1955).

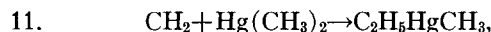
¹⁴ Carson, Carson, and Wilmshurst, *Nature* **170**, 320 (1952).

¹⁵ Hartley, Pritchard, and Skinner, *Trans. Faraday Soc.* **46**, 1019 (1950).

¹⁶ H. O. Pritchard, *J. Chem. Phys.* **25**, 267 (1956).

¹⁷ Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc. (London)* **A218**, 269 (1953).

to Steps 1–3 and 5–7 in the mechanism of the inhibited decomposition (Steps 4, 8, and 9 are, of course, not relevant here). The following additional steps are included:



Steps 10–12 were not included in the mechanism for the inhibited reaction because of their lesser importance in the presence of excess C₅H₁₀. In connection with Steps 10 and 11, no direct evidence for the product C₂H₅HgCH₃ was obtained; the infrared spectrum of the "undecomposed residue" from the decomposition of DMM (carried out to 24% decomposition) showed no bands other than those of DMM.

As the extent of decomposition is increased, certain other reactions apparently occur, producing the observed C₃ and C₄ hydrocarbons; these may include the following: CH₂ + C₂H₆ → C₃H₈, CH₂ + C₂H₄ → C₃H₆, CH₂ + C₃H₆ → C₄H₈, CH₃ + C₂H₆ → CH₄ + C₂H₅, 2C₂H₅ → C₄H₁₀, 2C₂H₅ → C₂H₄ + C₂H₆.

A steady-state solution of the partial mechanism (Steps 1–3, 5–7, inclusive) yields the following equations:

$$(CH_3) = [k_1(DMM)/k_6]^{1/2}; \quad (5)$$

$$-\frac{d(DMM)}{dt} = k_1(DMM) \left\{ 1 + \left[\frac{(k_3 + k_6)^2(DMM)}{k_1k_6} \right]^{1/2} \right\}; \quad (6)$$

$$\frac{d(CH_4)}{dt} = k_3 \left(\frac{k_1}{k_6} \right)^{1/2} (DMM)^{3/2}; \quad (7)$$

$$\frac{d(C_2H_6)}{dt} = k_1(DMM) \left[1 + \frac{k_6}{(k_1k_6)^{1/2}} (DMM)^{1/2} \right]. \quad (8)$$

From Eq. (6) one may approximate the ratio of k_D for the uninhibited decomposition to k_1 ($=k_D$ for the fully inhibited reaction) using the following estimated values of the rate constants (in cc/mole sec):

$$k_3 = 2.5 \times 10^{11} \exp(-10000/RT),^{18}$$

$$k_6 = 1.0 \times 10^8 \exp(-2000/RT),^{19}$$

$$k_1 = 2.1 \times 10^{12} T^{1/2}.^{20}$$

For $T = 300^\circ\text{C}$ and $(DMM) = 1.7 \times 10^{-6}$ mole/cc, one calculates $k_D/k_1 = 18$, which may be compared to the observed value of 11, based on the present measurements of k_D for the uninhibited decomposition. At

¹⁸ Obtained³ by combining data of reference 13 with that of R. Gomer and G. B. Kistiakowsky, *J. Chem. Phys.* **19**, 85 (1951).

¹⁹ From a two-point fit of the data of Gomer and Kistiakowsky (see reference 18), i.e., $\log k_3/k_6$ vs $1/T$.

²⁰ Gomer and Kistiakowsky (reference 18); also G. B. Kistiakowsky and E. K. Roberts, *J. Chem. Phys.* **21**, 1637 (1953).

550°C and (DMM) = 3×10^{-9} mole/cc (approximately the conditions of Gowenlock *et al.*¹⁷) one calculates a ratio of 1.01, consistent with the lack of toluene inhibition noted by these authors.

From these equations one also obtains a semiquantitative prediction of the increase in the ratio of ethane to methane yields as the temperature is raised. The calculations are very sensitive to the values of the estimated rate constants; they serve only to show that an increase of two orders of magnitude in the ratio would be expected between the 300°C conditions and those of the high-temperature experiments of reference 17 (cf. observed ratios in the range 0.03–0.2 at 300°C vs 5 at 620°C).

The activation energy for methane formation is approximated to be $E_3 + (E_1 - E_6)/2 \cong 39$ kcal/mole, which is in rather poor agreement with the present apparent methane activation energy of 44.7 kcal/mole. This is perhaps not unexpected since the mechanism predicts 3/2 order formation of CH₄. In the present study no information on the order with respect to CH₄ was obtained; apparent first-order constants were calculated and an average (DMM) used in evaluating E_M .

The present mechanism suggests that in the low-temperature region one should observe a trend in the order of the rate constant for DMM loss from 3/2 to 1 as the temperature increases. A trend in the opposite direction has been noted in the literature.^{8,21} It is apparent that a careful re-investigation of the kinetic order (both DMM loss and CH₄ formation) for the uninhibited decomposition is needed in this connection. In addition, the mechanism offers no explanation for the lower activation energy (51 kcal/mole) found by Gowenlock *et al.*¹⁷ and Price and Trotman-Dickenson²² in the high-temperature region where the reaction is essentially nonchain.

Extrapolation of the present Arrhenius plot for the uninhibited decomposition to the higher temperature region leads to a line which lies somewhat above the

²¹ Yeddapanalli, Srinivasan, and Paul, *J. Sci. Ind. Research (India)* **13B**, 232 (1954).

²² S. J. Price and A. F. Trotman-Dickenson, *Trans. Faraday Soc.* **53**, 939 (1957). These authors noted the strong pressure dependence of the rate constant for the decomposition of DMM in the high-temperature region.

literature data (references 17 and 22). The difference is thought to be due to the pressure effect on the unimolecular rate constant. The present inhibited experiments were carried out at total pressures of ca 300 mm Hg, compared to values (for references 17 and 22) less than 20 mm Hg; as seen from Fig. 4, only small corrections to the present rate constants are needed to obtain the limiting high-pressure values. The temperature dependence of the pressure effect on the unimolecular rate constant is expected²³ to give rise to a low apparent energy of activation for experiments at low pressures. It is suggested that this is a factor responsible in part for the difference²⁴ between the present results and those of references 17 and 22.

ACKNOWLEDGMENTS

The authors appreciate the financial support of this work by the Michigan Memorial Phoenix Project, the U. S. Atomic Energy Commission Division of Research [Contract AT(11-1)-321], and the Alfred P. Sloan Foundation.

²³ N. B. Slater, *Phil. Trans. Roy. Soc. London Ser. A* **246**, 57 (1953); see also A. F. Trotman-Dickenson, *Gas Kinetics* (Butterworths Publications, Ltd., London, 1955), p. 63.

²⁴ Although only limited data on the pressure dependence of k are available, one may estimate n , the effective number of normal vibrations in the Slater theory; then it is possible to make a rough prediction of the difference between the activation energy for the high-pressure unimolecular constant and the apparent activation energy deduced from low-pressure rate constants: $E_0 - E_p = nRT/2$, where E_0 is the activation energy for the unimolecular rate constant and E_p is that for the rate constant in the fully bimolecular region. From the present data the ratio P_0/P_{50} (Slater's notation) is estimated to be (very approximately) 650 mm Hg/9 mm Hg = 72, which corresponds to $n \cong 11$ [Table 4 of reference 23 (Slater)]. Alternatively, in terms of the shift of a curve of $\log k/k_\infty$ vs $\log P$ at two temperatures, $n = 2\Delta \log P / \Delta \log T$. From a plot of $1/k$ vs $1/P$ for the data at 816°K (reference 22, Fig. 1) $k_\infty \cong 1.5 \text{ sec}^{-1}$; from this a plot of $\log k/k_\infty$ vs $\log P$ may be constructed and compared with a similar one for the present data (632°K). After extrapolation to allow overlap, a shift corresponding to $n \cong 10$ is noted. [A third estimate of n based on the magnitude of $k/k_\infty = I_n(\theta)$ using Slater's²³ relation for θ/P and his Table 3, requires more information than available. The factors except f_n are known; unfortunately the high pre-exponential factor gives rise to a very atypical value of θ/P and the results are unsatisfactory.] Choosing $n = 10$ as a minimum estimate, $E_0 - E_p \geq 8$ kcal/mole near 800°K. Since Price and Trotman-Dickenson²² used as their standard pressure a value (16 mm Hg) where the slope of the log-log plot corresponded to an order of ca 1.5, the difference in activation energy would of course be smaller than this value (and probably somewhat smaller than the 7 kcal/mole discrepancy sought).