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# Hydrogen-Chloride-Catalyzed Pyrolysis of Dimethyl Ether and the Use of HCl Catalysis for Diagnosis of Complex Chains\*

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The pyrolysis of CH<sub>3</sub>OCH<sub>3</sub>, catalyzed by gaseous HCl (3 to 16 mole %) has been studied in the temperature range 452° to 483°C. The rate approaches independence of HCl at the higher concentrations and is 3/2 order in ether. The products are the same as in the uncatalyzed decomposition (CH<sub>4</sub>+CO+H<sub>2</sub> and  $CH_4+CH_2O$ ) and no HCl is consumed. From the observation that there is up to a tenfold acceleration in rate with HCl it is shown that the slow step in the uncatalyzed pyrolysis is the reaction

 $CH_3 + CH_3OCH_3 \rightarrow CH_4 + CH_2OCH_3$ .

The hitherto-conceived slow step

#### $CH_2OCH_3 \rightarrow CH_2O + CH_3$

resulting from the analysis of S. W. Benson and D. V. S. Jain [J. Chem. Phys. 31, 1008 (1959)] is instead very rapid, and thus CH2OCH3 cannot be an important chain breaker.

Recent data on the stability of HCO indicate that CH<sub>3</sub> and CHO are the actual chain-breaking radicals, both being important in the uncatalyzed decomposition. The H<sub>2</sub>S catalyzed reaction is discussed briefly and shown to be similar to the HCl system. HCl catalysis as a diagnostic tool in analyzing complex chains is discussed.

#### INTRODUCTION

THE free-radical processes in the thermal decomposition of dimethyl ether have been represented by Benson and Jain<sup>1</sup> in the following step reactions:

$$CH_{3}OCH_{3} \xrightarrow{1} CH_{3}+CH_{3}O,$$

$$CH_{3}+CH_{3}OCH_{3} \xrightarrow{2} CH_{4}+CH_{2}OCH_{3},$$

$$CH_{2}OCH_{3}+(M) \xrightarrow{3} CH_{3}+CH_{2}O+(M),$$

$$CH_{3}O \xrightarrow{4} CH_{2}O+H,$$

$$H+CH_{3}OCH_{3} \xrightarrow{6} H_{2}+CH_{2}OCH_{3},$$

$$H+CH_{2}O \xrightarrow{7} H_{2}+CHO,$$

$$CH_{3}+CH_{2}O \xrightarrow{8} CH_{4}+CHO,$$

$$CH_{3}+CH_{2}O \xrightarrow{9} CO+H+(M),$$

$$CH_{3}+H_{2} \xrightarrow{10} CO+H+(M),$$

$$CH_{3}+H_{2} \xrightarrow{10} CH_{4}+H,$$

$$12$$

$$2CH_{3} \xrightarrow{10'} CH_{3}CH_{2}OCH_{3},$$

$$CH_{3}+CH_{2}OCH_{3} \xrightarrow{10''} (CH_{2}OCH_{3})_{2}.$$

The foregoing scheme extended the simpler Rice-Herzfeld-type mechanism originally suggested by Benson<sup>2</sup> by inclusion of both the CH<sub>3</sub> and CH<sub>2</sub>OCH<sub>3</sub> radicals in the termination processes. Benson and Jain predicted that methyl ethyl ether and dimethoxyethane would be present in amounts comparable to the ethane. Anderson and Benson<sup>3</sup> measured the trace products of the ether system and found they were much smaller than predicted. Most of the difference was accounted for by considering the steady-state value of these trace ethers. The remaining discrepancy was near the limits of the analytical precision. If the difference were real, then the mechanism would require alteration.

In the scheme the principal chain involves Step 2 and Step 3, whose rates were assumed to be about equal, making the CH<sub>2</sub>OCH<sub>3</sub>/CH<sub>3</sub> ratio near unity. On this basis, if Step 2 were replaced by a process which removed CH<sub>3</sub> many times faster than Step 2, then Step 3 would become the slow step whose rate would increase as the CH<sub>2</sub>OCH<sub>3</sub> radical concentration increases. If by such a process all the CH<sub>3</sub> radicals were converted to CH<sub>2</sub>OCH<sub>3</sub> radicals, the maximum rate increase would be a factor of two. Conversely, any acceleration significantly greater than twofold means that Step 2 must be slower than Step 3. This is a simple diagnostic test for the assumption of Benson and Jain and for the slow step of the chain. The hydrogen chloride catalysis, which has not been previously reported, was used in this study.

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<sup>1</sup> S. W. Benson and D. V. S. Jain, J. Chem. Phys. 31, 1008 (1959).
<sup>2</sup> S. W. Benson, J. Chem. Phys. 25, 27 (1956).
<sup>3</sup> K. H. Anderson and S. W. Benson, J. Chem. Phys. 36, 2320 (1962).

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TABLE I. Data summary for Me<sub>2</sub>O/HCl system.

Run	(Me <sub>2</sub> O/HCl) <sub>0</sub>	Temp. (°C)	$(P_T)_0$ (mm Hg)	$\begin{array}{c} k_{j} \times 10^{6} \\ (\text{mm Hg}^{-\frac{1}{2}} \\ \text{sec}^{-1}) \end{array}$	Order
3	20.3	480	180	25	<u></u>
9	22.6	483	314	55	
10	22.6	484	60.8	24	
12	36.1	456	486	20	1.24
14	36.1	456	35	20	(12/14)*
15	34.6	456	549	21	1.36
17	34.6	456	14	120	(13/17)
18	10.5	452	490	47	1.25
19	10.5	452	6.1	180	(18/19)
20	5.75	456	485	49	1.40
21	5.75	456	16	58	(20/21)
Jain	•••	456	•••	4.28	

<sup>a</sup> Runs compared in Eq. (2) are shown in parentheses.

#### EXPERIMENTAL

The vacuum line used was basically the same as in previous work.<sup>3</sup> The analytical reagent-grade dimethyl ether which was obtained from Matheson Company, Inc., was introduced into the vacuum line and purified before storing by bulb-to-bulb distillation. It was redistilled prior to use. Hydrogen chloride was also purchased in analytical reagent grade from Matheson Company, Inc. It was introduced into the vacuum line, purified by bulb-to-bulb distillation and stored in a blackened vessel. Some yellowing appeared after prolonged storage but was not present in samples redistilled just prior to use. Analysis by gas chromatography indicated that the impurities were less than 0.01 mole % and 0.1 mole % in the hydrogen chloride and dimethyl ether, respectively.

Mixtures of hydrogen chloride and dimethyl ether were prepared in a mixing vessel of about 2-liter capacity. Hydrogen chloride was admitted first and measured against a spoon gauge fitted with a sensitive capacitive null detector.<sup>3</sup> A premeasured amount of dimethyl ether was placed in a trap adjoining the hydrogen chloride. Both gases were condensed independently and allowed to mix on warming, with about one hour being required for complete mixing. The mixtures were then introduced into the reaction cell and pressure-time measurements made.

Product analyses, which turned out to be similar to those found with pure dimethyl ether,<sup>3</sup> showed no new peaks in the gas chromatographic analysis. Trace products which were done only qualitatively did not show any MeOEt but did show a trace amount of  $C_2H_6$  and a small amount of dimethoxyethane. CO,  $H_2$ , CH<sub>4</sub>, HCl, CH<sub>2</sub>O, and undecomposed ether were the main products, and they appeared in amounts consistent with the stoichiometry curve determined by Benson and Jain.<sup>1</sup> Hydrogen chloride was determined by difference after being absorbed on Auramine

# $\{[(CH_3)_2NC_6H_4]_2CNH\},\$

which showed that it was not consumed within 2% to 5%. The system was studied at about 456 °C over a range of 3% to 16% added HCl as shown in Table I.

## RESULTS

From the pressure-time data and the Benson-Jain stoichiometry curve<sup>1</sup> the amount of dimethyl ether present in the system at any time was determined. Integrated rate plots showed that the decomposition was equally well represented over the first 40% by orders ranging from first to 5/2. By comparing a number of runs of differing starting pressures  $P_1$  and  $P_2$ for  $(\Delta P)_0=0.05$ , the order, *n*, as shown in Table I was calculated from

$$(\Delta P_1/\Delta t)/(\Delta P_2/\Delta t) = (\bar{P}_1/\bar{P}_2)^n.$$
<sup>(2)</sup>

3/2-order rates have been used to evaluate the system, and by comparison with Jain's rate<sup>1</sup> the catalyzed rate is about ten times faster. This is in good agreement with the work of Imai and Toyama,<sup>4</sup> who observed a rate increase of about eight times when the pyrolysis of dimethyl ether was catalyzed by hydrogen sulfide.

In this system the hydrogen chloride furnished chlorine atoms which abstract hydrogen from the ether at least a hundred times faster than does methyl radical. Since the catalytic effect on the rate was about tenfold, then Step 2 is the slow step in the basic ether chain and the ratio  $\theta = CH_2OCH_3/CH_3$  is of the order of 0.1. This revised value for  $\theta$  brings the trace termination products into good agreement.<sup>3</sup> However, it implies that the [1+X] term of the Benson and Jain rate law<sup>1</sup> will contribute only about one tenth as much, which leads to predicted activation energies that are too low. That is, the experimental value is 55.6 kcal, while the rate law,

$$\left[-d(\mathrm{Me_2O})/dt\right]_0 = k_0 \left[\mathrm{Me_2O}\right]^{\frac{1}{2}}/\left[1+X\right],\qquad(3)$$

where  $X = (k_{10''} k_2 / k_{10} k_3)$  predicts only about 50 kcal.

Thus the HCl catalysis results imply that CH<sub>2</sub>OCH<sub>3</sub> is not an important chain terminator and some other species must be found.

### ROLE OF FORMYL RADICAL

Recent work on the formyl radical has led to a reconsideration of its role in the dimethyl ether decomposition. The older values for  $\Delta H_f^0$ (HCO) by appearance potentials and kinetic analysis are -4.4 to -9.0kcal and 11.2 kcal, respectively. Shannon and Harrison<sup>5</sup>  $^{-4}$ N. Imai and O. Toyama, Bull. Chem. Soc. Japan 34, 328 (1961). <sup>5</sup> T. W. Shannon and A. G. Harrison, Can. J. Chem. 40, 1392 (1961). reviewed these values and report a new value obtained from appearance potentials of  $-0.3\pm3.0$  kcal. Based on a new value for the C-H bond energy in CH<sub>3</sub>CHO reported by O'Neal and Benson,<sup>6</sup> the kinetic value adopted here is  $\Delta H_f^0(\text{HCO}) = 7.0$  kcal. This in turn means that D(H-CO) is now up 4 kcal, making D(H-CO) = 19 kcal. However,  $\Delta C_p$  for this reaction is about 4.0 cal/mole-°K, so that at 780°K, D(H-CO) =21 kcal. An increase of 6 kcal for the process HCO+ $M \rightarrow \text{H}+\text{CO}+\text{M}$  makes the HCO concentration comparable to CH<sub>3</sub> and thus eligible to participate in the termination processes. A value of  $E_9 \simeq 23$  kcal has been derived in this work for the decomposition of HCO, in very good agreement with the above estimate.

Further evidence for the importance of HCO in this system comes from the studies on the  $H_2CO$  decomposition. At temperatures near 415°C pure  $H_2CO$  pyrolyzes to yield mainly CO and CH<sub>3</sub>OH with very little  $H_2$ .<sup>7-9</sup> The absence of large amounts of  $H_2$  indicates that the HCO chain must have a high activation energy and does compete favorably with the processes that form CH<sub>3</sub>OH.

Thus for  $CH_2O$  pyrolysis the propagation steps below 400°C are

$$CHO+CH_{2}O \xrightarrow{c} CO+CH_{2}OH,$$
$$CH_{2}OH+CH_{2}O \xrightarrow{d} CH_{3}OH+CHO.$$

Above 400°C Reaction e must compete with c:

$$CHO+M \rightarrow CO+H+M.$$

## MODIFICATION OF MECHANISM

Replacing Steps 10' and 10'' as significant terminators by similar reactions with the formyl radical we write:

$$Me+CHO \xrightarrow{13'} CH_4+CO,$$
  
$$2CHO \xrightarrow{13''} H_2+CO.$$
(4)

Term	Coefficient	Energy difference (kcal)	Contri- bution (kcal)
E	1	50.0	50.0
$(G/N)(E_8-E_2)$	0.44	-3.3	-1.4
$(W/Y)(E_9-E_8)$	0.41	17.0	7.0
(WW'/Y) (E <sub>9</sub> -E <sub>8</sub> +E <sub>6</sub> -E <sub>7</sub> )	0.04	15.0	0.6
$E_{expl}(est'd)$	•••	•••	56.2

<sup>8</sup> E. O'Neal and S. W. Benson, J. Chem. Phys. **36**, 2196 (1962). <sup>7</sup> W. D. Walters and J. E. Longfield, J. Am. Chem. Soc. **77**, 6098 (1955). <sup>8</sup> C. J. M. Fletcher, Proc. Roy. Soc. (London) A146, 357 (1934).

<sup>•</sup> <sup>9</sup> J. G. Calvert and E. W. R. Steacie, J. Chem. Phys. 19, 176 (1951).

By following the stationary-state procedure we obtain the relative ratios:

$$\phi = \frac{(\mathrm{H})}{(\mathrm{Me})} = \frac{k_{8}(\mathrm{CH}_{2}\mathrm{O}) + k_{11}(\mathrm{H}_{2})}{k_{6}(\mathrm{Me}_{2}\mathrm{O}) + k_{12}(\mathrm{CH}_{4})},$$
  

$$\theta = \frac{(\mathrm{CH}_{2}\mathrm{O}\mathrm{CH}_{3})}{(\mathrm{Me})} = \frac{k_{2}(\mathrm{Me}_{2}\mathrm{O})}{k_{3}(\mathrm{M})} \left(1 + \frac{k_{6}}{k_{2}}\phi\right),$$
  

$$\omega = \frac{(\mathrm{CHO})}{(\mathrm{Me})} = \frac{k_{8}(\mathrm{CH}_{2}\mathrm{O})}{k_{9}(\mathrm{M})} \left(1 + \frac{k_{7}}{k_{8}}\phi\right),$$
  

$$\psi = \frac{(\mathrm{MeO})}{(\mathrm{Me})} = \frac{k_{5}(\mathrm{CH}_{2}\mathrm{O})}{k_{4}(\mathrm{M})}\phi.$$
 (5)

Setting the rate of initiation equal to the rate of termination of radicals we obtain for methyl:

$$(Me) = \lfloor (k_1/k_{10}) (Me_2O) \rfloor^{\frac{1}{2}} \\ \times \left\{ 1 + \left(\frac{k_{13'}}{k_{10}}\right)^{\frac{1}{2}} \left[\frac{k_8(CH_2O)}{k_9(M)}\right] \left[1 + \frac{k_7(CH_2O)}{k_6(Me_2O)}\right] \right\}^{-1}, \\ = \lfloor (k_1/k_{10}) (Me_2O) \rfloor^{\frac{1}{2}} [1 + \omega]^{-1}, \quad (6)$$

where  $(k_{13''}/k_{10})^{\frac{1}{2}}$  is taken as unity.

The accompanying rate law is

$$\frac{d(\mathbf{Me}_{2}\mathbf{O})}{dt} = \frac{k_{2} \left(\frac{k_{1}}{k_{1c}}\right)^{\frac{1}{2}} \left[\mathbf{Me}_{2}\mathbf{O}\right]^{\frac{1}{2}} \left\{1 + \frac{k_{8}(\mathbf{CH}_{2}\mathbf{O})}{k_{2}(\mathbf{Me}_{2}\mathbf{O})} + \frac{k_{11}(\mathbf{H}_{2})}{k_{12}(\mathbf{CH}_{4})}\right\}}{\left\{1 + \left(\frac{k_{13''}}{k_{10}}\right)^{\frac{1}{2}} \left[\frac{k_{8}(\mathbf{CH}_{2}\mathbf{O})}{k_{9}(\mathbf{M})}\right] \left[1 + \frac{k_{7}(\mathbf{CH}_{2}\mathbf{O})}{k_{6}(\mathbf{Me}_{2}\mathbf{O})}\right]\right\}}.$$
 (7)

The activation energy corresponding to this rate law is found as the logarithmic derivative of the rate constant with respect to temperature to be

$$E_{\text{exptl}} = E_0 + \frac{G}{N} (E_8 - E_2) + \frac{H}{N} (E_{11} - E_2) + \frac{W}{Y} (E_9 - E_8) + \frac{WW'}{Y} (E_9 - E_8 + E_6 - E_7), \quad (8)$$

where the symbols used for the coefficients of each term are defined as follows:

----

$$E_{0} = [E_{2} + \frac{1}{2}(E_{1} - E_{10})],$$

$$N = [1 + k_{8}(CH_{2}O) / k_{2}(Me_{2}O) + k_{11}(H_{2}) / k_{2}(Me_{2}O)] \cong 1.81,$$

$$G = [k_{8}(CH_{2}O) / k_{2}(Me_{2}O)] \cong 0.8,$$

$$H = [k_{11}(H_{2}) / k_{2}(Me_{2}O)] \cong 0.01,$$

$$Y = [1 + k_{8}(CH_{2}O) / k_{9}(M) + k_{8}k_{7}(CH_{2}O)^{2} / k_{9}k_{6}(Me_{2}O)(M)] \cong 1.77,$$

$$W = [k_{8}(CH_{2}O) / k_{9}(M)] \cong 0.7,$$

$$W' = [k_{7}(CH_{2}O) / k_{6}(Me_{2}O)] \cong 0.1.$$
(9)

Table II shows the activation energy contributions of the significant terms. These contributions bring the estimated activation energy into good agreement with the observed value. Not all rate constants of this system are known independently and the following procedure of evaluation was used.

Dropping minor terms<sup>10</sup> in Eq. (7) the rate law may be written

Rate/
$$k_0$$
 (Me<sub>2</sub>O)  $= (1+G)/(1+W)$ . (10)

It was previously observed that CH<sub>2</sub>O accelerated the rate so that (1+G)/(1+W) > 1. The autocatalysis of the ether decomposition is due mainly to CH<sub>2</sub>O and by comparing the 3/2-order rate constants  $k_0$  and  $k_{0.1}$  at initial and 10% reaction, respectively, reported by Benson and Jain<sup>1</sup> then we find  $(1+G)/(1+W) = 1.05 \pm 0.05$ . By calculating G from known rate constants and concentrations over 10% reaction, W=0.7 was estimated. From this  $E_9$  is found to be 23 kcal which is in good agreement with the endothermicity range associated with the energy-transfer process for the decomposition of formyl radical. This implies that the addition of H to CO at 25°C has an activation energy of about 2 kcal.

# MECHANISM OF HYDROGEN CHLORIDE CATALYSIS

The effect of added HCl in the system is to replace the  $CH_3$  attack of Step 2 by a rapid Cl atom attack on the ether, followed by Step 3 for the decomposition of the ether radical. The CH<sub>3</sub> radical attacks HCl more than a hundred times faster than it attacks Me<sub>2</sub>O to reproduce the Cl atom. Secondary chains on CH<sub>2</sub>O are also set up. CH<sub>2</sub>OCH<sub>3</sub> and HCO radicals build up in system and are the important terminators. Needed steps in the chains are

$$Me + HCl \xrightarrow{a} CH_4 + Cl,$$

$$Cl + CH_3OCH_3 \xrightarrow{2n} HCl + CH_2OCH_3,$$

$$Cl + CH_2O \xrightarrow{8n} HCl + HCO,$$

$$H + HCl \xrightarrow{16} H_2 + Cl \qquad (11)$$

and in the termination, reactions are

$$2CH_{2}OCH_{3} \xrightarrow{10^{\prime\prime}} (CH_{2}OCH_{3})_{2},$$

$$2CHO \xrightarrow{13^{\prime\prime}} CO + H_{2},$$

$$HCO + CH_{2}OCH_{3} \xrightarrow{13^{\prime}} CO + CH_{3}OCH_{3}.$$
 (12)

Utilizing the steady-state approximation the following relations are obtained for the radicals of the system:

$$\frac{(\operatorname{Cl})}{(\operatorname{Me})} = \frac{k_{a}(\operatorname{HCl})}{k_{2a}(\operatorname{Me}_{2}\operatorname{O}) \left[1 + \frac{k_{8a}(\operatorname{CH}_{2}\operatorname{O})}{k_{2a}(\operatorname{Me}_{2}\operatorname{O})} + \frac{k_{b}(\operatorname{CH}_{4})}{k_{2a}(\operatorname{Me}_{2}\operatorname{O})} + \frac{k_{16}(\operatorname{H}_{2})}{k_{2c}(\operatorname{Me}_{2}\operatorname{O})}\right]} \cong \frac{k_{a}(\operatorname{HCl})}{k_{2a}(\operatorname{Me}_{2}\operatorname{O})Q},$$

$$(\text{where } Q \simeq 1)$$

$$\frac{(\operatorname{H})}{(\operatorname{Me})} = \frac{k_{8}(\operatorname{CH}_{2}\operatorname{O})}{k_{6}(\operatorname{Me}_{2}\operatorname{O})} \left[1 + \frac{k_{8a}k_{a}(\operatorname{HCl})}{k_{2a}k_{8}(\operatorname{Me}_{2}\operatorname{O})Q} + \frac{k_{16}k_{a}(\operatorname{HCl})(\operatorname{H}_{2})}{k_{2a}k_{8}(\operatorname{Me}_{2}\operatorname{O})Q}\right]} \cong \frac{k_{8}(\operatorname{CH}_{2}\operatorname{O})Q'}{k_{6}(\operatorname{Me}_{2}\operatorname{O})},$$

$$(\text{where } Q' > 1 \text{ and additive terms are significant})$$

$$\frac{(\operatorname{CHO})}{(\operatorname{Me})} = \frac{k_{8}(\operatorname{CH}_{2}\operatorname{O})}{k_{9}(\operatorname{M})} \left[1 + \frac{k_{7}(\operatorname{H})}{k_{8}(\operatorname{Me})} + \frac{k_{8a}(\operatorname{Cl})}{k_{8}(\operatorname{Me})}\right],$$

$$(\text{where additive terms are significant})$$

$$\frac{(\operatorname{CHO}_{2}\operatorname{OCH}_{3})}{(\operatorname{Me})} = \frac{k_{2}(\operatorname{Me}_{2}\operatorname{O})}{k_{3}(\operatorname{M})} \left[1 + \frac{k_{2a}(\operatorname{Cl})}{k_{2}(\operatorname{Me})} + \frac{k_{6}(\operatorname{H})}{k_{2}(\operatorname{Me})}\right].$$
(13)
$$(\text{where additive terms are significant})$$

$$The rate law$$

$$-\frac{d(Me_{2}O)}{dt} = k_{2}(Me_{2}O)(Me) \left[ 1 + \frac{k_{2a}(Cl)}{k_{2}(Me)} + \frac{k_{6}(H)}{k_{2}(Me)} \right]$$
$$= k_{2}(Me_{2}O)(Me) \left[ 1 + \frac{k_{a}(HCl)}{k_{2}(Me_{2}O)Q} + \frac{k_{8}(CH_{2}O)Q'}{k_{2}(Me_{2}O)} \right] (14)$$

<sup>10</sup> Elimination of the H<sub>2</sub> contribution H in the numerator N, is justifiable since it makes less than 1% contribution. In the denominator Y,  $k_9$  and  $k_6$  are not known, but a maximum value of unity is placed on the ratio  $k_7/k_6$  which means that an error of about 4% is introduced when WW' is eliminated from Y.

correctly predicts the catalysis by HCl. Evaluation of the expressions in Eq. (13) indicate that Cl and H are small compared to Me, being about 0.001. Me, CHO, and CH<sub>2</sub>OCH<sub>3</sub> are all of the same order of magnitude and all important terminators. The correct 3/2 order for Me<sub>2</sub>O in Eq. (14) is derived by setting the rate of the initiation process equal to that of the termination processes of Steps 10, 10', 10'', 13'; and 13'' shows (Me) being proportional to (Me<sub>2</sub>O)<sup>‡</sup>. Thus,

$$(Me) = \frac{(k_1/k_{10})^{\frac{1}{2}}(Me_2O)^{\frac{1}{2}}}{(1+D)^{\frac{1}{2}}},$$
(15)

where the contributions due to CH<sub>2</sub>OCH<sub>3</sub> and CHO are:

$$D = \frac{k_{10'}(CH_{3}OCH_{3})}{k_{10}(Me)} + \frac{k_{10''}(CH_{2}OCH_{3})^{2}}{k_{10}(Me)^{2}} + \frac{k_{13'}(CHO)}{k_{10}(Me)} + \frac{k_{13''}(CHO)^{2}}{k_{10}(Me)^{2}}.$$
 (16)

#### H<sub>2</sub>S CATALYZED DECOMPOSITION

There is excellent agreement in the experimental results between this work and that of Imai and Toyama.<sup>4</sup> In a discussion of their results they consider:

$$CH_{3}OCH_{3} \rightarrow CH_{3}O + CH_{3}, [1]$$

$$CH_{3} + CH_{3}OCH_{3} \rightarrow CH_{4} + CH_{2}OCH_{3}, [3]$$

$$CH_{3} + H_{2}S \rightarrow CH_{4} + HS, [6]$$

$$HS + CH_{3}OCH_{3} \rightarrow H_{2}S + CH_{2}OCH_{3}, [7]$$

$$CH_{2}OCH_{3} + (M) \rightarrow CH_{2}O + CH_{3} + (M), [4]$$

$$HS + HS \rightarrow \text{products}, [8]$$

$$CH_{3} + CH_{3} \rightarrow C_{2}H_{5}, [5] \qquad (17)$$

where the notation of Imai and Toyama is shown in bracketed numerals for the step reactions. In the catalyzed system Step a' and 2b replace Step 2. This is analogous to the HCl system.

For ether decomposition they write a simple Rice-Herzfeld rate,

$$R_{\rm Me20} = k_2 (k_1/k_{10})^{\frac{1}{2}} [{\rm Me}_2 {\rm O}]^{\frac{3}{2}}, \qquad (18)$$

where from their experiments they set,

$$k_2(k_1/k_{10})^{\frac{1}{2}} = 10^{13.66} \exp(-54\ 500/RT)$$
 (19)

in units of liter mole sec. While in the presence of  $H_2S$  the rate law is

$$R_{\rm H_{2S}} = k_{2b} (k_1/k_t) \,^{\frac{1}{2}} [{\rm Me_2O}]^{\frac{1}{2}}, \tag{20}$$

where the rate constants are taken as

$$k_{2b}(k_1/k_t)^{\frac{1}{2}} = 10^{13.76} \exp(-51\ 800/RT) \qquad (21)$$

in units of liter mole seconds.

Equation (19) predicts the untenable values for  $D(CH_3-OCH_3)\simeq 91$  kcal and  $A_1\simeq 10^{20}$  sec<sup>-1</sup> as well as  $A_{-1}\simeq 10^{13}$  liter<sup>4</sup> mole<sup>-4</sup> sec<sup>-1</sup> for the back reaction of Step 1 which led Benson and Jain<sup>1</sup> to alter the rate of Eq. (18). Further,  $D(CH_3-OCH_3)\simeq 81$  kcal based on thermodynamic estimates leads to 50 kcal activation energy in Eq. (18). Thus added H<sub>2</sub>S would raise the

Step reaction	log <sub>10</sub> kª (at 780°K)	$\log_{10} A$	E (kcal)	Source
1	-5.2	17.5	81.0	This work <sup>b</sup>
-1	10.7	10.7	0	This work°
2	5.8	8.5	9.5	d
3	6.8°	12	19.0	This work <sup>f</sup>
4	•••		22.0	g
7	9.5	10.0	2.0	h
8	6.7	8.5	6.2	i
9	5.8	12 <sup>i</sup>	23	This work
10	10.36	10.36	0	k
11	5.6	8.5	10.0	1
12	7.4	9.6	8.0	m
a	•••	9.23	4.5	n
b		10.5	3.9	0

<sup>a</sup> Units of liter mole seconds.

<sup>b</sup> Calculated using the rate law in Eq. (7).

<sup>c</sup> Calculated using the new value for  $k_1$  and the thermodynamic data estimates of Benson and Jain.<sup>1</sup>

<sup>d</sup> Reference 11.

<sup>e</sup> Assumed  $k_2/k_3 \simeq 0.1$ . <sup>f</sup> Reference 12.

<sup>g</sup> Reference 1.

<sup>h</sup> R. Klein, J. R. McNesby and M. D. Scheer, J. Chem. Phys. 32, 1814 (1960).

<sup>i</sup> K. O. Kutschke and S. Toby, Can. J. Chem. 37, 672 (1959).

<sup>1</sup> E. Whittle and E. W. R. Steacie, J. Chem. Phys. 21, 993 (1953).

<sup>in</sup> Calculated from  $k_{11}$  assuming  $\Delta S_{11}=4$  cal/mole and  $\Delta H_{11}=2$  kcal/mole.

<sup>n</sup> H. O. Pritchard, J. B. Pyke, and A. F. Trotman-Dickenson, J. Am. Chem. Soc. 77, 2629 (1955).

<sup>o</sup> A. F. Trotman-Dickenson, J. H. Knox, and G. C. Fettis, Can. J. Chem. 38, 1643 (1960).

activation energy by 1.8 kcal contrary to the experiments. Such simple limiting rate expressions must be expanded to properly account for the complexities due to  $CH_2O$ .

The catalysis by  $H_2S$  is quite similar to that of HCl and in the mechanism we choose the steps of Eq. (17) as well as,

$$HS+CH_{2}O \rightarrow H_{2}S+HCO,$$
  

$$HS+CH_{4} \rightarrow H_{2}S+CH_{3},$$
  

$$HS+H_{2} \rightarrow H_{2}S+H.$$
 (22)

The relative steady-state values of the radicals over about 5% reaction which are analogous to Eq. (13)

vield,

$$\frac{(\mathrm{HS})}{(\mathrm{Me})} \simeq \frac{k_{a'}(\mathrm{H_2S})}{k_{2b}(\mathrm{Me_2O})} \simeq 20,$$

$$\frac{(\mathrm{H})}{(\mathrm{Me})} \simeq \frac{k_{8b}k_{a'}(\mathrm{H_2S})(\mathrm{CH_2O})}{k_{8}k_{2b}(\mathrm{Me_2O})^2} \simeq 0.1,$$

$$\frac{(\mathrm{CHO})}{(\mathrm{Me})} \simeq \frac{k_{8b}k_{a'}(\mathrm{H_2S})(\mathrm{CH_2O})}{k_{9}k_{2b}(\mathrm{Me_2O})(\mathrm{M})} \simeq 100,$$

$$\frac{(\mathrm{CH_2OCH_3})}{(\mathrm{Me})} \simeq \frac{k_{a'}(\mathrm{H_2S})}{k_{3}(\mathrm{M})} \simeq 10.$$
(23)

The rate in the presence of H<sub>2</sub>S may be written,

$$R_{\rm H_{2S}} = k_{2b} (\rm Me_{2}O) (\rm HS) \left[ 1 + \frac{k_{2} (\rm Me)}{k_{2b} (\rm HS)} + \frac{k_{2} (\rm Me)}{k_{6} (\rm H)} \right]$$
  

$$\cong k_{2b} (\rm Me_{2}O) (\rm HS).$$
(24)

As with the HCl case, the radicals involved in chain breaking are proportional to  $(Me_2O)^{\frac{1}{2}}$  and the choice of the termination process is complicated by HS, CH<sub>2</sub>OCH<sub>3</sub>, and CHO all being important. In the case of termination by HS and CHO then,

(HS) = 
$$\frac{(k_1/k_l)^{\frac{1}{2}} (\text{Me}_2\text{O})^{\frac{1}{2}}}{\{1 + [k_{8b}(\text{CH}_2\text{O})/k_9(\text{M})]\}}$$
. (25)

Estimates of the additive term in the denominator indicate that Imai and Toyama's derived value of  $\log_{10} k_{2b} = 11 - (6800/RT)$  may be seven times too large.

## INDIVIDUAL RATE CONSTANTS

From the HCl catalysis it was concluded that  $\theta =$ CH<sub>2</sub>OCH<sub>3</sub>/CH<sub>3</sub> $\simeq$ 0.1 which means  $k_2/k_3 \simeq$ 0.1. Steacie<sup>11</sup> has studied Step 2 and using Marcus's<sup>12</sup> value  $E_3 = 19$ kcal, then  $A_3 \simeq 10^{12}$ . It has already been noted by Benson<sup>1</sup> that  $\Delta H_3 \simeq 7$  kcal, making  $E_{-3} \simeq 12$  kcal for the addition of  $CH_3$  to  $CH_2O$ .

By the rate law of Eq. (7) and using the notation defined in Eq. (9) the rate constant is expressed as

$$k_{\rm exp} = k_2 (k_1/k_{10})^{\frac{1}{2}} N/Y.$$
 (26)

Benson and Jain<sup>1</sup> determined that  $\log_{10} k_{exp} = 13.61 -$ 55 600/4.575T in units of liters<sup>1</sup> mole<sup>-1</sup> sec<sup>-1</sup> and in this study N=1.81 and Y=1.77. Using the data for  $k_{2}^{11}$  and  $k_{10}^{13}$  in Eq. (26) we obtain,

$$\log_{10} k_1 = 17.5 - 81\ 000/4.575T\ (sec^{-1}).$$
 (27)

This is down by a factor of three from Jain's value<sup>1</sup> and leads to a better value for the back reaction. That is,

$$\log_{10} k_{-1} = 10.7$$
 (liter/mole·sec)

with  $E_{-1}=0$ . For reference, the rate parameters and the rate constants at 780°K used in this study are listed in Table III.

<sup>11</sup> A. F. Trotman-Dickenson and E. W. R. Steacie, J. Chem. Phys. **19**, 329 (1951). <sup>12</sup> R. A. Marcus, B. deB. Darwent, and E. W. R. Steacie, J. Chem. Phys. **16**, 987 (1948). <sup>13</sup> E. K. Roberts and G. B. Kistiakowsky, J. Chem. Phys. **21**, <sup>15</sup>(27) (1052).

1637 (1953).