[CONTRIBUTION FROM BUREAU OF MINES]

The Pyrolysis of Formaldehyde[1,2]

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The pyrolysis of formaldehyde is shown to occur predominantly by a chain reaction. Carbon monoxide and hydrogen are formed in accordance with second-order rate laws. Methyl alcohol results from a homogeneous bimolecular reaction. An unspecified condensation product, amounting to a small fraction of the reacted formaldehyde, is also indicated. The thermal decomposition of mixtures of CH_2O and CD_2O gives H_2, D_2 and HD in proportions such that $P^2_{HD}/P_{H_2}P_{D_2}$ is a constant equal to about 3.6. The pyrolysis of CH_2O and D_2 mixtures shows that the hydrogen atom concentration, although small, exceeds that which would arise from the thermal decomposition of hydrogen alone.

Introduction

On the basis of pressure measurements, Fletcher[4] concluded that the decomposition of formaldehyde between 500 and 600° proceeded by a bimolecular, homogeneous process. Patat and Sachsse,[5] using an ortho-parahydrogen technique, estimated the steady-state H atom concentration to be 10^{-4} of the value computed on the basis of a Rice-Herzfeld scheme and inferred that a chain mechanism was not applicable. However, the work of Longfield[6] on the sensitized decomposition of formaldehyde suggests the existence of a reaction chain. The present investigation was undertaken to determine unambiguously whether or not formaldehyde decomposes thermally by a chain mechanism.

Results

If in the hydrogen isotope species formed in the decomposition of mixtures of CH_2O and CD_2O little or no HD is present, the mechanism for the formaldehyde pyrolysis would certainly not involve a chain process. A series of experiments was carried out in which 1:1 mixtures of CH_2O and CD_2O were pyrolyzed (the method of formaldehyde preparation and gas handling has been described elsewhere[7]), and the hydrogen isotope distribution in the reaction products was determined. The experimental results are given in Table I. Substantial quantities of HD are formed. Samples of the formaldehyde residue after a 30-second run gave the following analysis[8]: CH_2O, 45.2%; CD_2O, 50.6%; CHDO, 4.2%. The CHDO found is due completely to the CHDO present in the original CD_2O sample. There is, therefore, no isotope mixing between formaldehydes.

The kinetics of the pyrolysis of formaldehyde is such that it is independent of the surface to volume ratio of the reaction vessel. An increase of the S/V ratio by a factor of 16 or 35 has little, if any, effect on the rate.[4,6] We have confirmed these observations, using fused silica reaction vessels differing in their S/V ratios by a factor of 9. The decomposition rates are, however, sensitive to the previous history and treatment of the reaction bulb. The rates of pressure rise increase, although not regularly, as the number of runs increase. The most consistent data were obtained after the reaction vessel had been vacuum baked at 800° prior to a run. In Table II, experiments 1 through 4 were made with baked out bulbs while in 1a and 4a about 20 runs had been made previously without a bake out.

Table II also shows the course-of-reaction data. $P_{CO} - P_{H_2}$ is taken as methanol. We have identified it as a product of the reaction mass spectrometrically. Longfield had previously demonstrated conclusively that it occurs in the pyrolysis of formaldehyde. If the pyrolysis gave only CO, H_2 and CH_3OH as products, P_{H_2} should equal ΔP. P_{H_2} is always somewhat larger than ΔP, indicating a condensation reaction. The characterization of this condensation is not clear; it is, however, small.

TABLE I

HYDROGEN ISOTOPE DISTRIBUTION IN NON-CONDENSABLES FROM DECOMPOSITION OF CH_2O–CD_2O MIXTURES AT 547° AND 140 MM. TOTAL PRESSURE[a]

Expt. No.	$\frac{P_{CH_2O}}{P_{CD_2O}}$	Time, min.	P_{H_2}[b]	P_{D_2}[b]	P_{HD}[b]	$\frac{P^2_{HD}}{P_{H_2}\,P_{D_2}}$
1	1	0.5	44.6	11.6	43.8	3.7
2	1	1.0	43.9	12.7	43.4	3.4
3	1	5.0	40.3	14.4	45.3	3.5
4	1	30.0	32.5	18.4	49.1	4.0
5	5	2.0	84.7	0.6	14.7	4.2
6	0.2	5.0	9.8	51.2	39.0	3.0

[a] CD_2O, 96% in D, prepared from a deuterated polymer supplied by Tracerlab, Inc. [b] Parts per 100 of the total hydrogen isotopes produced. Analyzed with Consolidated Model 21–610 mass spectrometer.

An upper limit for the H-atom concentration during the pyrolysis of formaldehyde was determined. This was done by pyrolyzing a 10 to 1 mixture of CH_2O to D_2[9] at 165 mm. total pressure at 547°. Mass spectrometric analysis of the hydrogen isotopes at the end of one minute gave D_2, 14.7%; HD, 0.5%; H_2, 5.8%. The H-atom concentration was determined under the assumptions that (1) $^1/_2 P_{H_2}$ (final) is a good approximation for the time average of P_{H_2} in a one minute run, (2) HD arises from the exchange between H_2 and

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[2] Presented at 127th meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, March 29 to April 7, 1955, in Cincinnati, Ohio.

[3] (a) Olin-Mathieson Corp., New Haven, Conn.; (b) General Electric Co., Cincinnati, Ohio.

[4] C. J. M. Fletcher, *Proc. Roy. Soc.* (*London*), **A146**, 357 (1934).

[5] (a) F. Patat and H. Z. Sachsse, *Z. Elektrochem.*, **41**, 493 (1935).

[6] J. E. Longfield, Thesis, University of Rochester, 1951.

[7] M. D. Scheer, "Fifth Symposium (International) on Combustion," Reinhold, 1955.

[8] These analyses were performed through the courtesy of A. G. Sharkey and R. A. Friedel on a Consolidated Model 21-102 mass spectrometer.

[9] D_2, purified by diffusion through a palladium thimble, analyzed 99.8% D_2, 0.2% HD.

D_2 only. The interaction of D with H_2CO is neglected. The H-atom concentration so calculated necessarily represents an upper limit. It can be shown that in a mixture of H_2 and D_2, the initial rate of HD formation is proportional to the atom concentration[10].

TABLE II

COURSE OF REACTION FOR FORMALDEHYDE PYROLYSIS AT 547° IN THE REGION OF 140 MM.

Expt. No.	$P_{CH_2O(initial)}$, mm.	Time, min.	ΔP, mm.	$P_{cond.}$[a] mm.	P_{CO}, mm.	P_{H_2}, mm.	P_{CH_3OH} (P_{CO} −, P_{H_2}), mm.
1	138.6	1.0	12.1	108.7	24.2	17.3	6.9
2	142.2	2.0	21.0	100.4	36.6	26.2	10.4
3	141.8	5.0	34.3	79.6	57.3	39.2	18.1
4	141.5	10.0	49.2	62.8	75.6	52.3	23.3
1a	139.7	1.0	20.3	102.2	31.9	25.9	6.0
4a	136.1	10.0	87.2	34.4	100.2	88.7	11.5

[a] Reaction products condensable at −195°.

Therefore

$$\frac{[(H) + (D)]}{[(H) + (D)]_{thermal}} = \frac{\left(\frac{dP_{HD}}{dt}\right)_{t=0}}{\left(\frac{dP_{HD}}{dt}\right)_{t=0,\ thermal}}$$

where [(H) + (D)] refers to the atom concentration in the CH_2O–D_2 mixture and $[(H) + (D)]_{thermal}$ refers to the atom concentration in a hypothetical D_2–H_2 mixture undergoing purely thermal exchange at 547°. This mixture is presumed to have the same D_2 pressure and one-half the final hydrogen pressure as developed in the CH_2O–D_2 mixture.

$$\left(\frac{dP_{HD}}{dt}\right)_{t=0,\ thermal} = 4 \times 10^{-3} \text{ mm./min.}$$

and

$$\left(\frac{dP_{HD}}{dt}\right)_{t=0} = 0.5 \text{ mm./min.}$$

This gives an upper limit

$$[(H) + (D)] = 125\ [(H) + (D)]_{thermal} = 4.6 \times 10^{-8} \text{ mm.}$$

Discussion

There is little doubt that the decomposition of formaldehyde occurs by a chain mechanism. The evidence is (1) the formation of considerable HD from CH_2O–CD_2O mixtures in the absence of exchange; (2) the effect of the nature of the surface on the reaction; and (3) the radical sensitized decomposition of formaldehyde.[6] Table I shows the approximate constancy of the ratio $P^2_{HD}/P_{H_2}P_{D_2}$, about 3.6, over a 25-fold variation of the initial P_{CH_2O}/P_{CD_2O} ratio. This, together with the fact that mixed formaldehydes do not exhibit isotopic exchange in pyrolysis, excludes a bimolecular reaction as the mechanism of decomposition. The latter leads to a value $P^2_{HD}/(P_{H_2}P_{D_2})$ of one or less depending on whether a bimolecular HD forming reaction between CH_2O and CD_2O would give only HD or HD, H_2 and D_2. Clearly, formaldehyde decomposes thermally by a chain process.

The independence of the rate of the pyrolysis with respect to surface to volume ratio requires chain initiation and termination to be both either in the gas phase or at the wall. The difference in rate between "aged" vessels and vacuum baked vessels, together with the well established fact that termination in the photochemical decomposition of formaldehyde involves breaking at the walls,[11] strongly suggest that initiation and termination in the thermal decomposition are wall effects.

Fletcher has shown that the initial pressure dependence of the formaldehyde pyrolysis follows an approximately second-order rate law. If the second-order kinetics are maintained throughout the reaction, it can be shown that

$$\frac{1}{\Delta P} = \frac{1}{P_{H_2}} = \frac{1}{P_{CO}} \approx \frac{1}{F_0^2kt} + \frac{1}{F_0}$$

where F_0 is the initial formaldehyde pressure and k is a second-order rate constant. The linearity of the plot of the reciprocals of ΔP, P_{H_2} and P_{CO} with the reciprocal of time, Fig. 1, confirms the hypothesis. It may be noted that because of methanol formation, the straight line plot does not extrapolate to $1/F_0$ on the ordinate.

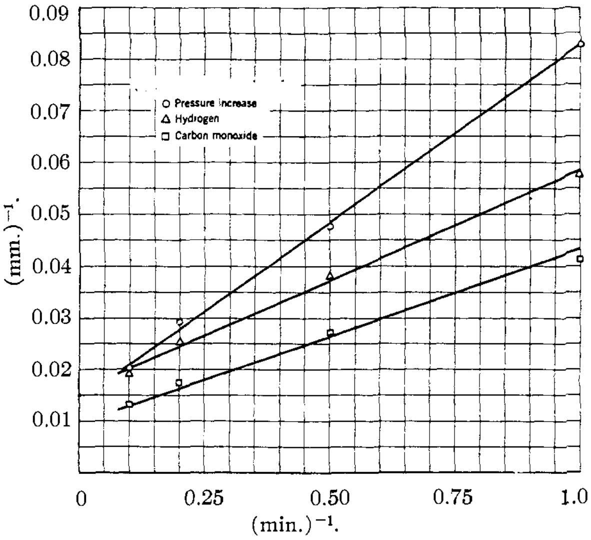

Fig. 1.—The pyrolysis of formaldehyde at 547° initially at 140 mm. pressure.

Methanol has been shown by Longfield to form in the formaldehyde decomposition by a second-order, possibly non-chain, reaction. We have confirmed these observations indirectly. Methanol, measured by $P_{CO} - P_{H_2}$, follows second-order kinetics since CO and H_2 are produced by second-order processes. The rate of its formation is independent of the extent of surface. If methanol is formed by a homogeneous non-chain reaction, second order in formaldehyde, less methanol is expected the faster formaldehyde is consumed in a concomitant chain process. Comparison of 1 and 1a, and 4 and 4a, Table II, shows that less methanol is produced in the faster reactions. This constitutes evidence that methanol arises from a non-chain, homogeneous process in the thermal decomposition of formaldehyde.

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[10] R. Klein, M. D. Scheer and L. J. Schoen, THIS JOURNAL, **78**, 47 (1956).

[11] J. G. Calvert and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 176 (1951).

Table I shows the approximate constancy of the ratio $P^2_{HD}/(P_{H_2}P_{D_2})$ over a 25-fold variation of the initial P_{CH_2O}/P_{CD_2O} ratio. Kinetically this implies, assuming formation of the molecular hydrogen species by interaction of a radical with a formaldehyde molecule, that the radical concentration is directly proportional to the appropriate formaldehyde concentration. That is, if

$$\frac{dP_{HD}}{dt} = k[(D)(H_2CO) + (H)(D_2CO)],$$

$$\frac{dP_{H_2}}{dt} = k[(H)(H_2CO)] \text{ and } \frac{dP_{D_2}}{dt} = k[(D)(D_2CO)]$$

then

$$\frac{P_{HD}}{P_{H_2}P_{D_2}} = \frac{[(D)(H_2CO) + (H)(D_2CO)]^2}{[(D)(D_2CO)][(H)(H_2CO)]}$$

is a constant equal to 4 only if D and H are proportional to the first power of D_2CO and H_2CO, respectively. We have neglected the difference in rates due to isotope effects, although their inclusion would not alter the argument.

A scheme for the thermal decomposition of formaldehyde, consistent with the data and observations, is

$$CH_2O + CH_2O \xrightarrow{K_1 \text{ wall}} HCO + H + CH_2O \quad (I)$$

$$HCO \xrightarrow{k_2} H + CO \quad (II)$$

$$H + H_2CO \xrightarrow{k_3} H_2 + HCO \quad (III)$$

$$HCO \xrightarrow{K_4 \text{ wall}} \text{products} \quad (IV)$$

There is derived from the mechanism

$$\frac{dP_{H_2}}{dt} = \frac{dP_{CO}}{dt} = \frac{d\Delta P}{dt} = -\frac{dP_{CH_2O}}{dt} = \frac{K_1k_3}{K_4} P^2_{CH_2O}$$

Stoichiometrically, $CH_2O = CO + H_2$. P_{H_2} exceeds ΔP somewhat because of an unspecified condensation reaction. However, as shown in Table II, it is relatively small.

From the mechanism, and with the available data, it is possible to estimate k_3

$$P_H = \frac{K_1k_2}{k_3K_4} P_{CH_2O}$$

$$P_H = 4.6 \times 10^{-8} \text{ mm.}$$

$$\frac{1}{P_{H_2}} = \frac{1}{(P_{CH_2O})_0} + \frac{K_4}{(P_{CH_2O})_0 K_1k_2t}$$

From the slope of the $1/P_{H_2}$ *versus* $1/t$ plot of Fig. 1

$$\frac{K_1k_2}{K_4} = 2 \times 10^{-5} \text{ (mm.)}^{-1} \text{ sec.}^{-1}$$

$$\frac{K_1k_2}{k_3K_4} = 3 \times 10^{-10}$$

Therefore

$$k_3 = 7 \times 10^4 \text{ (mm.)}^{-1} \text{ sec.}^{-1}$$

On the basis of collision theory, an upper limit for the activation energy of the $H + H_2CO \rightarrow H_2 + HCO$ reaction is calculated as 5.7 kcal. This agrees with the upper limit estimates of other investigators.[12]

(12) K. H. Geib, *Ergeb. Exakt. Naturwiss.*, **15**, 44 (1936).

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[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

Kinetics of the Hydrogen Fluoride Catalyzed Alkylation of Toluene by *t*-Butyl Chloride[1]

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Further measurements have been made on the reaction of *t*-butyl chloride and toluene as catalyzed by hydrogen fluoride. The reaction rate is greatly retarded by hydrogen chloride. The effect of five promoters was studied. It was found necessary to modify the equations and theory of Pearlson and Simons[5] to correlate the rate measurements in any one experiment. The mechanism postulated for the reaction explains all of the experimental facts. It is essentially a proton transfer mechanism.

Previous kinetic studies[4,5] of the alkylation reaction between toluene and *t*-butyl chloride as catalyzed by hydrogen fluoride present strong evidence against any ionic or free radical intermediates for this reaction. Two variations of a proton transfer mechanism in an amphoteric medium are presented.

The previous work[4,5] had shown that the rate of this reaction is proportional to the first power of the concentrations of reactants, and a high power (6-7) of the catalyst pressure. In addition, it was found that the rate is greatly increased by the presence of extremely small amounts of organic oxygen-containing compounds. An extension of these measurements appeared highly desirable. In the present work the effect of catalyst pressure was studied at three temperatures. The effect of five promoters also was studied.

Experimental

Preparation of Materials.—The reactants and catalyst were prepared as previously described.[5]

Anhydrous hydrogen chloride was prepared by dropping degassed, concentrated sulfuric acid (m.p. 10.0-10.5°) onto sodium chloride (C.P.) in an evacuated system. The gas was dried by passage through anhydrous calcium chloride at −77°.

The promoters used were 2-fluoropyridine, trimethylacetic acid, trifluoroacetic acid, silver trifluoroacetate and water. 2-Fluoropyridine was prepared by the diazotization of 2-aminopyridine in hydrogen fluoride solution.[6] The product was distilled through an efficient fractionating column and a middle cut of constant index of refraction was stored over anhydrous potassium carbonate. Trimethylacetic acid (Eastman Kodak Co.) was distilled through an

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(1) Taken in part from the Ph.D. thesis of A. S. Gow, Jr., The Pennsylvania State University, 1954.

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(4) J. W. Spraner and J. H. Simons, THIS JOURNAL, **64**, 648 (1942).

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