According to Table I, the H/C ratio in the polymer is only slightly above unity, tending perhaps to be greatest for the smallest energy inputs. The mechanism suggested is consistent with such a result. Hydrogen produced as by reaction 3 would ultimately be balanced by production of an approximately equivalent amount of biphenyl.

As an alternative mechanism we may consider the possibility of a reaction like

$$C_6H_6^* + C_6H_6 \longrightarrow (C_6H_6)_2 \qquad (6a)$$

The dimer can be a radical and can add either to other normal benzene molecules in a relatively slow reaction or much more rapidly by the general process

$$(C_6H_6)_n + C_6H_6^* \longrightarrow (C_6H_6)_{n+1} \qquad (7)$$

It is required for reactions such as 7 that the excited molecule $(C_6H_6)^*$ be stable, even though reactive. Evidence for such stability has already been recounted.[16] A formally similar reaction has been postulated to account for certain peculiar features of the radiolytic polymerization of acetylene.[17]

An important feature which must be explained by any suggested mechanism for polymer formation is that $G(C_6H_6 \rightarrow \text{polymer})$ is independent both of intensity within a factor of two and of total energy. One might be tempted to associate this result with the constancy of $G(H_2) \sim 0.036$ over a great range of energy output and intensity,[3] but the fact is that $G(C_6H_6 \rightarrow \text{polymer})$ remains constant although G(double bonds) and the average molecular weight of polymer are both greatly dependent on total energy input but not on intensity. A satisfactory interpretation is that the initially excited benzene molecules which react inevitably to give polymer are those which are excited with a fixed probability to a definite energy level; the number of these molecules considerably exceeds those which are primarily decomposed to give hydrogen.

Although we have no clear-cut mechanism for formation of benzene polymer we are left with the conclusion that H atoms are not involved to an important extent.

It remains to speculate briefly about the nature of the polymer produced. Consider, for example, the polymer which contains an average of five molecules of benzene. According to Figs. 1 and 2 such an "average molecule" contains an average 0.6 double bond per benzene ring or about 3 double bonds per unit of polymer. A little experimentation will convince the reader that it is possible to draw several such "average molecule" structures, in which six-membered rings are attached to a partially saturated chain of the type suggested by the work of Gibson, Blake and Kalm.[9] However, in the present stage of our information it is not possible to make adequate test of such a structure against results or even to establish that such an "average molecule" is at all present in the polymer.

NOTRE DAME, INDIANA

[17] J. L. Magee and M. Burton, *J. Phys. Chem.*, **56**, 842 (1952).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE CATHOLIC UNIVERSITY OF AMERICA]

The Thermal Decomposition of Acetaldehyde[1]

BY FRANCIS OWEN RICE AND ROBERT E. VARNERIN

RECEIVED DECEMBER 31, 1953

When 50–50 mixtures of $CH_3CHO–C_2D_6$ or $CD_3CDO–C_2H_6$ are decomposed, the amount of isotopic mixing as measured by the CH_3D/CH_4 or CD_3H/CD_4 ratios is proportional to the fraction of aldehyde decomposed. When different amounts of NO are added to the aldehyde–ethane mixtures the ratios of CH_3D/CH_4 or CD_3H/CD_4 are (for constant fractional decomposition of the aldehyde) either independent of the concentration of NO or increase somewhat as the NO concentration increases. When 50–50 mixtures of $CD_3CDO–CH_3CH{=}CH_2$ and $CD_3CDO–C_2H_6$ are decomposed, the CD_3H/CD_4 ratio for a given fractional decomposition of aldehyde is 1.8:1 respectively for the two reactions. Our results indicate (1) that the thermal decomposition of CH_3CHO and CD_3CDO are similar, (2) that both are chain reactions unaccompanied by any significant amount of direct separation into product molecules and (3) that the thermal decomposition of a substrate in presence of an indicator (in which either the substrate or indicator is fully deuterated) provides a general method for studying elementary reactions.

1. Introduction

The thermal decomposition of acetaldehyde is a homogeneous reaction that proceeds at a measurable rate at about 500° according to the equation $CH_3CHO \rightarrow CH_4 + CO$, with almost complete absence of any complicating simultaneous reactions. Although the facts regarding the over-all change are not in dispute, the situation is very different with regard to the detailed mechanism. This may occur intramolecularly by migration of a hydrogen atom or by rupture of a carbon–carbon bond followed by a chain reaction such as suggested by Rice and Herzfeld.[2] Since the evidence for and against these views has been adequately summarized[3] we shall mention here only those aspects having a direct bearing on our own experiments.

In the thermal decomposition of acetaldehyde the presence of small quantities of NO (less than 1.0 mm.) has no appreciable effect on the rate if the initial aldehyde pressure is about 150 mm. but reduces the rate appreciably when the initial aldehyde pressure is about 50 mm.[4] For pressures of NO higher than about 2 mm. there is always a marked

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[1] This research was supported by the United States Air Force under contract no. 18(600)-64 monitored by the Office of Scientific Research.

[2] F. O. Rice and K. H. Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1946, pp. 120–129; C. N. Hinshelwood, "Kinetics of Chemical Changes," Clarendon Press, New York, N. Y., 1947, pp. 137–139.

[4] (a) L. A. K. Staveley and C. N. Hinshelwood, *J. Chem. Soc.*, 813 (1936); (b) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 246 (1942).

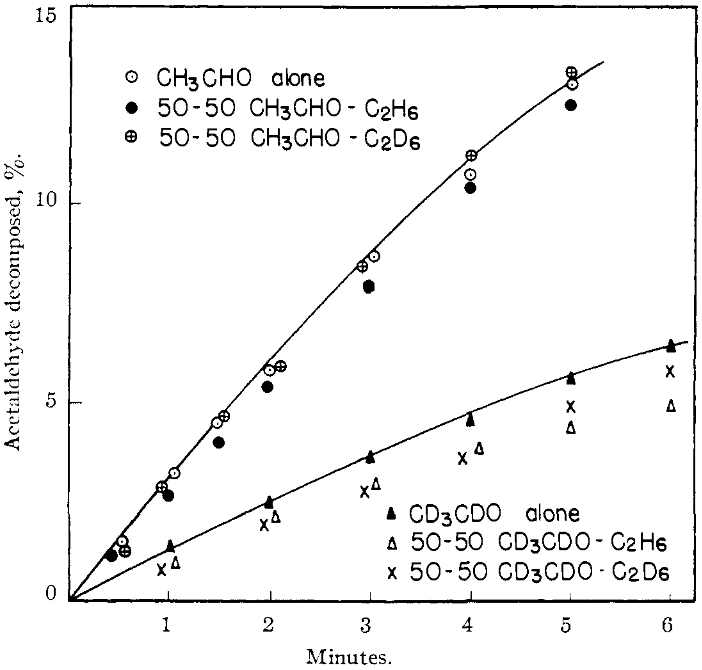

Fig. 1.—Thermal decomposition of CH_3CHO and CD_3CDO alone and in presence of an equal concentration of C_2D_6 and C_2H_6 at 508°; acetaldehyde pressure in all experiments was about 100 mm.; manometric measurements.

accelerating effect. Propylene[5] also has been found to inhibit the thermal decomposition of acetaldehyde.

In this paper we have attempted to determine whether the non-radical and the radical mechanism are both occurring to an appreciable extent in the thermal decomposition of acetaldehyde, using a method described in a previous paper.[6] Equimolecular mixtures of acetaldehyde and ethane-d^9 or acetaldehyde-d_4 and ethane were decomposed and the extent of mixing was determined by measuring, using the mass spectrometer, the values of the ratios CH_3D/CH_4 or CD_3H/CD_4, respectively, as a function of the fraction of acetaldehyde decomposed. It should be possible to obtain evidence regarding the simultaneous presence of chain and non-chain transformation by measuring the extent of mixing for a fixed fractional decomposition of substrate both alone and in presence of nitric oxide or propylene.

2. Experimental

The pyrolytic apparatus and the mass spectrometer used in this investigation have been described previously.[6] The C_2D_6, C_2H_6, CD_4, CH_4 and NO were the same as used in the previous investigation. The CD_3CDO[7] was heated to 300° before using so as to remove any paraldehyde present. CH_3CHO was prepared from J. T. Baker paraldehyde by pyrolysis at 300°. Mass spectrometer analysis of these compounds showed that the CD_3CDO was 99.6% deuterated and that paraldehyde was absent from both samples. Propylene was Matheson tank gas with a reported purity of 99% or greater.

All experiments were carried out in the temperature range 500–510° and an initial aldehyde pressure of about 100 mm. The temperature regulation within each experiment was ±0.1° or better. The per cent. decomposition of each sample was determined manometrically on the basis of the rise in pressure during the experiment, assuming that acetaldehyde decomposes into two product molecules. These values were checked by mass spectrometric analysis and were found to be quite accurate (1% or better).

The original mass spectrometer analyses were made of the entire sample containing all the decomposition products, as well as the undecomposed substrate and the indicator molecule. The sample was then cooled to liquid nitrogen temperature and the non-condensable products analyzed. We found that absorption of acetaldehyde in the mass spectrometer, especially in the stopcock grease in the gas inlet system caused errors which we avoided by repeating all the experiments but making analysis only on products not condensed at liquid nitrogen temperature. This reduced the experimental error in the analysis for the methanes and carbon monoxide. Accordingly, the extent of isotopic mixing was based largely on the extent of formation of the methanes. The analysis of the mixed methanes and of C_2D_5H has been described previously. Analysis for CD_2H_2 was not made in all experiments although it was detected in a few experiments in small quantities. Analysis for acetaldehyde-d_3 was made on the basis of the ion current on mass 47 corrected for $C^{13}CD_3O^+$ and for the 1.6% acetaldehyde-d_3 in the original sample. The acetaldehyde-d_1 analysis was made on the basis of the ion current on mass 45 corrected for $C^{13}CH_4O^+$. Analysis for ethane-d_1 was made on the basis of the ion current on mass 31 corrected for $C^{13}CH_6^+$. Analysis for propylene-d_1 was made on the basis of the ion current on mass 43 corrected for $C^{13}C_2H_6^+$ and for $C^{13}CDO^+$ from the spectrum of acetaldehyde-d_3.

All mass spectra were made from mass 2 to mass 50. In preliminary analyses the range was extended to mass 120 for several samples of all mixtures used in this investigation.

3. Thermal Decomposition of CH_3CHO and CD_3CDO.

—The rates of the thermal decomposition of CH_3CHO and CD_3CDO were measured manometrically at 508° and 100 mm. pressure of acetaldehyde. We found that CH_3CHO decomposes 2.4 times as fast as CD_3CDO, a value which is in good agreement with that found by R. E. Smith.[8] The experiments were repeated using 50–50 mixtures of CH_3CHO–C_2D_6 and CD_3CDO–C_2H_6. The presence of ethane has a slight inhibiting effect somewhat greater with CD_3CDO than with CH_3CHO. The results are shown in Fig. 1.

4. Effect of NO on the Rate of Decomposition of CH_3CHO and CD_3CDO.

—Previous work[9] had shown that at CH_3CHO pressures of 150 mm. and higher, NO, up to pressures of about 1 mm., had no appreciable effect but when the CH_3CHO pressure was 50 mm., pressures of NO in the neighborhood of 1 mm. reduced the rate of decomposition of CH_3CHO by about 10%. In all cases, increasing amounts of NO above one or two mm. caused rapid acceleration of the rate of decomposition of the CH_3CHO.

In our work the effect of nitric oxide on the thermal decomposition of CH_3CHO and CD_3CDO was studied manometrically at 505° and 100 mm. pressure of aldehyde. Under our conditions in the range of 1–7 mm. NO, there is a pronounced ac-

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(5) F. O. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 273 (1938).

(6) F. O. Rice and R. E. Varnerin, THIS JOURNAL, **76**, 324 (1954).

(7) We wish to thank Dr. Paul D. Zemany of the General Electric Research Laboratory for supplying us with a sample of this substance.

(8) R. E. Smith, *Proc. Far. Soc.*, **35**, 1328 (1939).

(9) (a) L. A. K. Staveley and C. N. Hinshelwood, *J. Chem. Soc.*, 812 (1936); (b) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A180**, 237 (1942).

celerating effect with CH_3CHO whereas with CD_3CDO there is a pronounced inhibition with a maximum at about 1.2 mm. followed by a rapid acceleration. The results are shown in Fig. 2. We made a few measurements at higher concentrations of NO and found that the effect of NO on CH_3CHO and CD_3CDO was very similar. The results, at higher NO pressures, are shown in Table I.

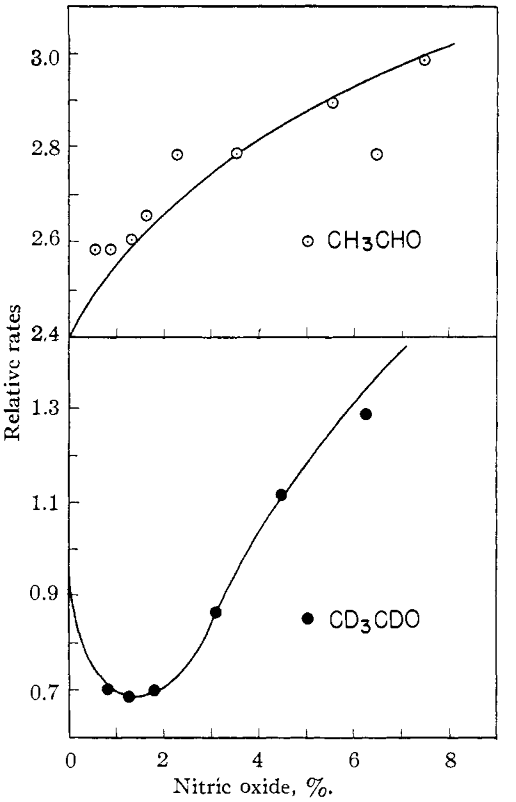

Fig. 2.—Thermal decomposition of CH_3CHO and CD_3CDO at 505° in presence of nitric oxide; initial aldehyde pressure 105 ± 5 mm.; manometric measurements.

TABLE I

RELATIVE RATES OF DECOMPOSITION OF CH_3CHO AND CD_3CDO IN PRESENCE OF LARGER ADDITIONS OF NO (TEMPERATURE 505°, ALDEHYDE PRESSURE (APPROXIMATELY) 100 MM.)

NO, %	CH_3CHO	CD_3CDO
0	2.4	1.0
7.5	3.81	..
9.9	..	1.52
13.0	..	1.74
16.0	4.10	..
17.8	..	1.85
24.0	4.66	..
25.1	..	2.07

5. Effect of Propylene on the Rate of Decomposition of CH_3CHO and CD_3CDO.—In a study of the inhibiting effect of propylene on various thermal decompositions, Rice and Polly[5] found that the addition of 100 mm. of propylene to 200 mm. of acetaldehyde at 500° reduced the rate to a little less than half of the uninhibited rate. Smith and Hinshelwood[4b] found the same effect occurred at 550°. In this paper working at 500° and 100 mm. pressure of aldehyde, we found that 50 mm. of propylene reduced the rate of CH_3CHO to 0.29 times the normal rate and reduced the rate of CD_3CDO to 0.15 times the normal rate. The results are shown in Fig. 3.

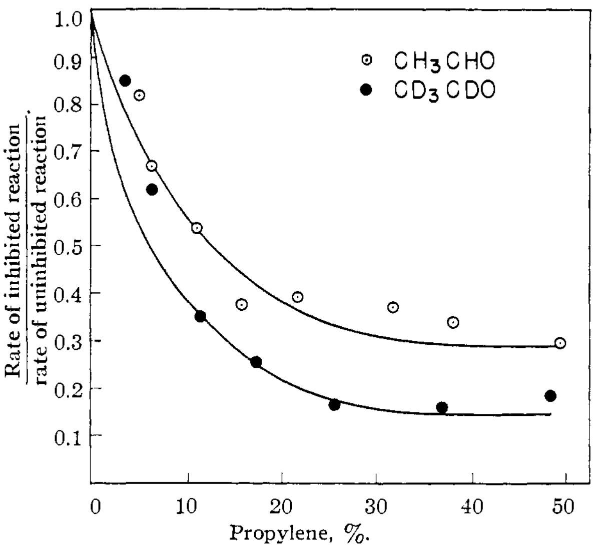

Fig. 3.—The propylene inhibition of the thermal decomposition of CD_3CDO and CH_3CHO at 505° and initial acetaldehyde pressure of about 100 mm.; manometric measurements.

6. Extent of Mixing with Indicators.—In a search for a stable indicator we first made experimental runs on 50–50 mixtures of CH_3CHO and CD_4 but found that the isotopic mixing was not extensive. In a typical experiment we found values of approximately 0.5 for $CH_3D/CH_4 \times 100$ when 20–30% of the CH_3CHO was decomposed. We then did experiments with ethane and found it was quite stable under the conditions of our experiment.[6] Mixtures of 50–50 $CH_3CHO–C_2D_6$ and 50–50 $CD_3CHO–C_2H_6$ gave satisfactory mixing over a range of 5–30% decomposition of the aldehyde and the practically complete absence of H_2, HD or D_2 proved that there was no appreciable sensitized decomposition of the ethane occurring under the conditions of our experiments.

Essentially no mixing occurs when 100 mm. of an equimolecular $C_2D_6–C_2H_6$ mixture is heated to 505° for 30 minutes in presence or absence of 22 mm. of NO. There is also no mixing when a similar $CH_3CH{=}CH_2—C_2D_6$ mixture is heated under the same conditions.

7. Thermal Decomposition of $CH_3CHO–C_2D_6$ and $CH_3CHO–C_2D_6$–NO Mixtures.—Equimolecular mixtures of $CH_3CHO–C_2D_6$ were decomposed alone and in presence of NO at 503 to 507° to various percentage decompositions of the CH_3CHO and the products were analyzed in the mass spectrometer. For 15% decomposition of the aldehyde we found the following values: CH_3D/CH_4, 0.032; C_2D_5H/C_2D_6, 0.015; acetaldehyde-d_1/acetaldehyde, 0.007. The isotopic mixing as determined by the CH_3D/CH_4 ratio was approximately proportional to the % CH_3CHO decomposed and was independent of the concentration of nitric oxide for low pressures of NO. For higher NO pressures and higher % decomposition of CH_3CHO, the mixing was greater than in absence of NO. The results are shown in Fig. 4.

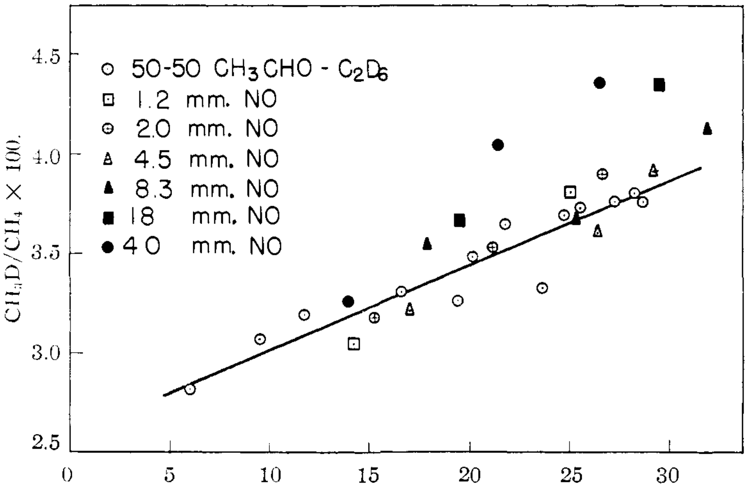

Fig. 4.—Thermal decomposition of 50–50 mixtures of CH_2CHO and C_2D_6 alone and in presence of nitric oxide at 500° and 80 to 100 mm. CH_3CHO; mass spectrometer measurements. Curve represents the decomposition in absence of NO.

8. Thermal Decomposition of CD_3CDO–C_2H_6 and CD_3CDO–C_2H_6–NO Mixtures.—Equimolecular mixtures of CD_3CDO and C_2H_6 were pyrolyzed alone and in presence of NO at 506° to various percentage decompositions of CD_3CDO. The products were analyzed on the mass spectrometer. For 10% decomposition of the aldehyde, the values of the following ratios are CD_3H/CD_4, 0.218; C_2H_5D/C_2H_6, 0.021; acetaldehyde-d_3/acetaldehyde-d_4, 0.099. The isotopic mixing as determined by the CD_3H/CD_4 ratio was proportional to the per cent. CD_3CDO decomposed but the presence of NO increased the value of the CD_3H/CD_4 ratio by about 5%. This increase was approximately independent of the concentration of NO. The results are shown in Fig. 5.

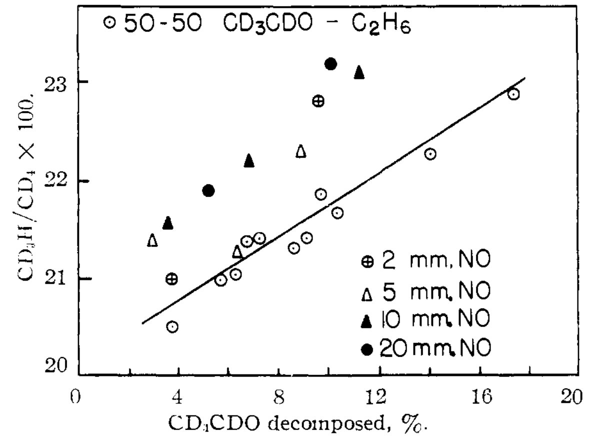

Fig. 5.—Thermal decomposition of 50–50 mixtures of CD_3CDO and C_2H_6 alone and in presence of nitric oxide at 504 ± 2° and 80 to 100 mm. initial pressure of CD_3CDO; mass spectrometer measurements. Curve represents the decomposition in absence of NO.

9. Thermal Decomposition of CD_3CDO–C_3H_6 and CD_3CDO–C_3H_6–NO Mixtures.—Equimolecular mixtures of CD_3CDO and $CH_3CH{=}CH_2$ were pyrolyzed alone and in presence of NO at 504° to various percentage decompositions of CD_3CDO and the products were analyzed on the mass spectrometer. The extent of mixing as determined by the CD_3H/CD_4 ratio was about 1.8 times as great as in the case of the CD_3CDO–C_2H_6 system. The CD_3H/CD_4 ratio was approximately proportional to the % CD_3CDO decomposed and was increased slightly by additions of NO. The results are shown in Fig. 6.

10. Discussion and Conclusions

As will be seen, especially from Figs. 4–6 inclusive, we have obtained no indication whatsoever of the presence of any direct migration of a hydrogen atom in CH_3CHO or a deuterium atom in CD_3CDO to give the products in a single elementary step.

There is a curious phenomenon that appears in Figs. 4 to 6 inclusive, namely, that the intercepts of the curves for per cent. of aldehyde decomposed against the CH_3D/CH_4 ratios on the ordinate have different finite values depending on the mixture used. Thus a 50–50 mixture of CH_3CHO–C_2D_6 has an initial CH_3D/CH_4 ratio = 2.55, which is the relative speeds of the two reactions, $CH_3 + C_2D_6$ and $CH_3 + CH_3CHO$. Relationships such as these for both acetaldehyde[10] and acetone[11] have been already noted but since this appears to be a general method for obtaining relative speeds of elementary reactions, we will defer any detailed discussion of the scope of the method to a later pa-

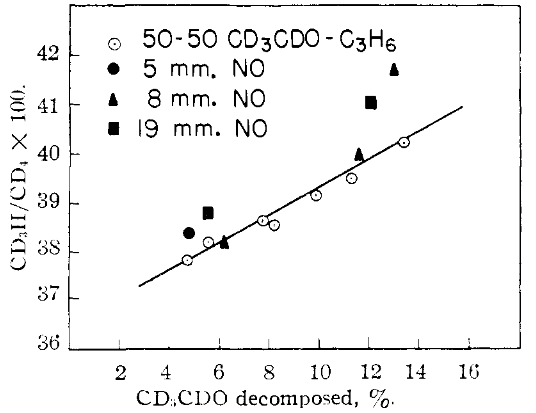

Fig. 6.—Thermal decomposition of 50–50 mixtures of CD_3CDO and C_3H_6 alone and in presence of nitric oxide at 504 ± 2° and 80 to 100 mm. initial pressure of CD_3CDO; mass spectrometer measurements. Curve represents the decomposition in absence of NO.

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[10] L. A. Wall and W. J. Moore, *J. Phys. Chem.*, **55**, 965 (1951).

[11] J. R. McNesby, T. W. Davis and A. S. Gordon, *J. Chem. Phys.*, **21**, 956 (1953).

per and include here only the results (Table II) obtained in this paper together with a comparison of published results. The published results for reactions 1, 4 and 5 are taken from a recent review by Trotman-Dickenson.[12] In the case of reactions 2 and 3 we have assumed that the activation energy is 1.8 kcal. greater than that of reactions 1 and 4, respectively. Since the literature values were obtained at lower temperatures using a very different technique, the differences from our values are not too surprising.

TABLE II

RELATIVE SPEEDS OF ELEMENTARY REACTIONS

$$CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \quad (1)$$

$$CD_3 + CD_3CDO \longrightarrow CD_4 + CD_3CO \quad (2)$$

$$CH_3 + C_2D_6 \longrightarrow CH_3D + C_2D_5 \quad (3)$$

$$CD_3 + C_2H_6 \longrightarrow CD_3H + C_2H_5 \quad (4)$$

$$CD_3 + CH_3CH{=}CH_2 \longrightarrow CD_3H + CH_2{=}CH{=}CH_2 \quad (5)$$

	Lit. val. rel. 12
$k_1/k_3 = CH_4/CH_3D = 39.2$	71.2
$k_2/k_4 = CD_4/CD_3H = 4.75$	11.7
$k_2/k_5 = CD_4/CD_3H = 2.75$	3.9

We would like to express our thanks to Dr. E. W. R. Steacie and to Dr. James R. McNesby for helpful discussion and suggestions in connection with this paper.

[12] F. A. Trotman-Dickenson, *Quart. Rev.*, **VII**, 198 (1953).

WASHINGTON, D. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Viscosity of Vapor Mixtures of Hydrogen Peroxide and Water

BY CHARLES N. SATTERFIELD, RALPH L. WENTWORTH AND STERGE T. DEMETRIADES

RECEIVED JANUARY 4, 1954

The viscosity of hydrogen peroxide–water mixtures in the vapor state, containing up to 65 mole % hydrogen peroxide, was measured by a capillary flow method at one atmosphere total pressure and at a temperature of 170°. By extrapolation, the viscosity of anhydrous hydrogen peroxide vapor at 170° was found to be 144 micropoises. A few studies also were made at 200 and 240° to provide a basis for estimating the effect of temperature. The results of this work may be expressed by the following equation: $\mu = 134 + 0.35(t - 100) - 14y$; where μ = viscosity, micropoises; t = temperature, and y = vapor composition, mole fraction hydrogen peroxide. This equation is recommended for the calculation of the viscosity of vapor mixtures of hydrogen peroxide and water over the temperature range of about 100 to 300°, and has a precision of within ±2%. The results provide a measure of the viscous forces in a highly polar gaseous mixture; few such systems have been studied previously.

The viscosity of vapor mixtures of hydrogen peroxide and water is of interest for at least two reasons: (a) The use of hydrogen peroxide as an energy source requires knowledge of such physical properties as vapor viscosity in the design of power producing devices. (b) Relatively little information is available on the transport properties of mixtures of two highly polar gases. No information previously has been published on the viscosity of this system in the vapor phase.

The method used here was that of measurement of the pressure drop occurring upon flowing hydrogen peroxide vapor through a capillary tube at constant temperature. The mathematical relation between the viscosity, μ, the measured pressure drop, Δp, and the volumetric flow rate, q, is given by the Poiseuille equation

$$\mu = 10^6 \pi r^4 (\Delta p)/8qL \qquad (1)$$

Equation 1 is valid only when the flow is streamlined in a tube of radius, r, and length, L. In practice the measured pressure drop will include contributions from energy losses at the entrance and exit of the tube. These must be minimized and corrected for to obtain the pressure drop due to viscous flow only, which is required for use in equation 1. The apparatus was therefore calibrated with gases of known viscosity.

The following alterations to equation 1 must be made in order that the viscosity may be calculated from the experimentally determined pressure difference, $p_1 - p_2$, and mass rate of flow, w: (a) Since the fluid under measurement is compressible, equation 1 must be integrated to allow for the changing value of the volumetric rate of flow as the fluid of molecular weight M having a compressibility factor z passes through the capillary tube. This results in the equation[1]

$$\mu = 10^6 \pi r^4 M(p_1^2 - p_2^2)/16LwRTz \qquad (2)$$

(b) A correction factor, K_E, which allows for kinetic energy losses, must be introduced in equation 2.

Apparatus and Procedure

Working with hydrogen peroxide vapor introduces several experimental difficulties: (a) Hydrogen peroxide vapor is highly reactive. Furthermore, at atmospheric pressure mixtures with inert gases containing above about 26 mole % hydrogen peroxide vapor will explode readily on contact with a wide variety of substances which are catalytically active,[2] particularly the metals of relatively high atomic weight. (b) Being a condensable vapor, care must be taken to avoid condensation and the presence of mist. (c) Decomposition of hydrogen peroxide into water and oxygen in the apparatus changes the composition of the system, introduces a third component, oxygen, and causes difficulty in temperature control.

The apparatus used in this work consisted of a boiler for producing hydrogen peroxide vapor, a separator and superheater for mist removal and temperature regulation, a capillary tube, and auxiliary equipment for the measurement of pressure, temperature and rate of flow. A rather complicated boiler is required to deliver at atmospheric pressure concentrated hydrogen peroxide vapor of a desired concentration and at a steady flow rate, and at the same time to minimize decomposition and to avoid explosions. Such a

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[1] G. Barr, "A Monograph of Viscometry," Oxford University Press, London, 1931, p. 153.

[2] C. N. Satterfield, G. M. Kavanagh and H. Resnick, *Ind. Eng. Chem.*, **43**, 2507 (1951).