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The Mechanism of the Thermal Decomposition of Ethane-d_6

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C_2D_6 decomposes at about one-third of the rate of C_2H_6 and is inhibited by NO. The inhibition curve for C_2D_6–NO mixtures is similar to that for C_2H_6–NO mixtures, the maximum reduction being to 18% and 8%, respectively, of the rate of the uninhibited reaction. When C_2D_6 is decomposed in the presence of an equal quantity of CH_4, the amount of isotopic mixing as measured by the CH_3D/CH_4 ratio, depends only on the fractional decomposition. When different amounts of NO are added to the C_2D_6–CH_4 mixture, the CH_3D/CH_4 ratio for constant fractional decomposition of the C_2D_6 is independent of the concentration of NO. Our results indicate that the thermal decomposition of ethane-d_6 is a chain reaction and that the direct separation of D_2 occurs to a negligibly small extent.

Introduction

The decomposition of ethane may occur (1) by the separation of H_2 in a single elementary act in accordance with the equation

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

or (2) by separation into two methyl radicals followed by a chain such as that postulated by Rice and Herzfeld.[3] There is the further possibility that both mechanisms may occur simultaneously to a measurable extent.

If the decomposition were purely intramolecular, it would be relatively easy to obtain conclusive experimental evidence. This could be done by decomposing, to a small extent, a mixture of C_2H_6 and C_2D_6 and analyzing the products in the mass spectrometer. If the reaction were entirely intramolecular, no compounds would be found which contained both hydrogen and deuterium. Unfortunately this experiment is conclusive only in the complete absence of any radical decomposition. If the chain reaction is present even to a small extent, there may be extensive mixing. For example, in the Rice–Herzfeld mechanism for the decomposition of ethane, the relatively stable chain radical CH_3CH_2 undoubtedly reacts with ethane according to the equation

$$CH_3CH_2 + C_2H_6 \longrightarrow C_2H_6 + CH_3CH_2$$

This regeneration reaction is of no importance in the decomposition of C_2H_6 but may cause extensive mixing when both C_2H_6 and C_2D_6 are present.

Hinshelwood[4] concluded from his work on the inhibition of the thermal decomposition of various substances by nitric oxide, that the fully inhibited reaction, which in the case of C_2H_6 had a rate constant approximately $^1/_{12}$ that of the uninhibited reaction, represents a situation in which the chain decomposition is entirely suppressed by the capture of all radicals by the nitric oxide. In an effort to settle this question, Hinshelwood and his coworkers[5] compared the maximum inhibition brought about by nitric oxide with the maximum inhibition brought about by propylene.[6] They found that in the cases of propylaldehyde, diethyl ether and *n*-pentane, the maximum inhibition brought about by nitric oxide and propylene was approximately the same. These experiments have led to the general acceptance of the idea that an intramolecular mechanism and a free radical mechanism occur simultaneously to an appreciable extent and the latter can be entirely suppressed by the addition of appropriate amounts of nitric oxide or propylene.

In a further attempt to settle this question some ingenious experiments were performed by Wall and Moore[7] using acetaldehyde, ethane and acetone. In a typical experiment, 50–50 mixtures of acetaldehyde and acetaldehyde-d_4 were decomposed to different extents and the products analyzed on the mass spectrometer. It was found that mixing occurred even in the earliest stages of the reaction. They further found that while the presence of nitric oxide inhibits the reaction rate and diminishes the isotopic mixing, the mixing still remains extensive even in the initial stages of the nitric oxide inhibited reaction but they concluded that part of the nitric oxide inhibited reaction proceeds intramolecularly and part as a free radical chain.

In contrast with the results of the work of Wall and Moore, a very careful study of the mechanism of acetone pyrolysis[8] in which 1:1.2 mixtures of deutero- and normal acetone were decomposed, showed that the mechanism is essentially free radical. Experimentally, it was found that the CD_3H/CD_4 ratio remained remarkably constant with time in spite of the fact that the acetone-d_5 ratio increased greatly. If the decomposition were appreciably intramolecular, the CD_3H/CD_4 ratio should increase markedly as the acetone-d_5/acetone-d_6 ratio increases whereas only a slow increase would be expected on the basis of a free radical mechanism.

Since this matter is of major importance in studying the kinetics of the thermal decomposition of organic compounds, we attempted to obtain an unequivocal answer by conducting a thermal decomposition in presence of a stable indicator. By having either the substrate or the indicator fully deuterated, it is possible by mass spectrometric analyses to measure the extent of mixing for a fixed fractional

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[1] This is taken from the dissertation presented by Robert E. Varnerin for the degree of Doctor of Philosophy in the Catholic University of America. The work was supported in part by the United States Air Force under Contract No. A. F. 18(600)-64 monitored by the Office of Scientific Research.

[2] Eastman Kodak Fellow, 1952–1953.

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

[4] L. A. K. Stavely and C. N. Hinshelwood, *Nature*, **137**, 29 (1936); *Proc. Roy. Soc. (London)*, **A154**, 335 (1936); *J. Chem. Soc.*, 812, 818 (1936); *Proc. Roy. Soc. (London)*, **A159**, 192 (1937); L. A. K. Staveley, *ibid.*, **A162**, 557 (1937); C. N. Hinshelwood, *J. Chem. Soc.*, 531 (1949).

[5] J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A180**, 237 (1942); F. J. Stubbs and C. N. Hinshelwood, *ibid.*, **A200**, 458 (1950).

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

[7] L. A. Wall and W. J. Moore, *J. Phys. Chem.*, **55**, 965 (1951); THIS JOURNAL, **73**, 2840 (1951).

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

decomposition of the substrate. If the generally accepted view is correct additions of nitric oxide should diminish the mixing, which should approach zero at maximum inhibition. If, on the other hand, the decomposition occurs wholly through a chain mechanism, additions of nitric oxide should have little or no effect on the extent of mixing for a given fractional decomposition of substrate. Our experiments are described in the following sections.

Experimental

The apparatus used in this investigation was the conventional static system for the study of reaction kinetics. The reaction vessel was of quartz, volume 30 cc., fitted with a 4 mm. thermocouple well and attached to a gas handling and high vacuum system by a graded seal. The temperature could be controlled manually to ±0.5° for extended periods.

The ethane (99.3%) and methane (99.8%) were Phillips research grade gases. The methane-d_4 was synthesized by Dr. Max Hellmann of the National Bureau of Standards and contained according to our analysis 85.5% CD_4, 0.9% CD_3H, 12% N_2 and 2.4% O_2. We removed the oxygen by passing the gas over heated sodium. The ethane-d_6 was synthesized by Dr. L. A. Wall[9] of the National Bureau of Standards by passing D_2O over calcium carbide and deuterating the acetylene-d_2 over a nickel catalyst. Mass spectrometric analysis showed 97.7% C_2D_6, 2.3% C_2D_5H and less than 0.1% of impurities. The nitric oxide was prepared by the nitrometer reaction. In a few runs tank nitric oxide containing about 10% nitrous oxide was used, but no difference could be detected from pure nitric oxide.

The mass spectrometric analyses were made in a modified Westinghouse sector field instrument with a 90° tube. Analysis for CH_3D was based on the height of the peak at mass 17, corrected for HO^+, $C^{13}H_4^+$ and CD_2H^+. Analysis for CD_3H was made on the basis of the ion current at mass 19, making a small correction for the spectrum of C_2D_6. Analysis for HD was made on the basis of the ion current for mass 3. Analysis for C_2D_5H was made on the basis of the ion current in mass 35. The contribution of the 2.3% C_2D_5H in the original sample and $CD_3C^{13}D_2^+$ were subtracted so that the analyses reported give the C_2D_5H formed during the pyrolysis. Wherever possible we determined sensitivities of the particular peaks used for analyses but in the case of CD_3H, for example, we used published data.[10]

Experimentally, CD_2H_2 is the most difficult of the methanes to analyze on the mass spectrometer because of the contributions of H_2O^+ and CD_3^+. We could not detect the presence of CD_2H_2 and, in any case, neglecting small percentages would not affect appreciably the analysis of CH_3D.

The percentage conversion was calculated solely on the basis of pressure changes during the course of the reaction. Checks were made on the accuracy of the method of studying the thermal decomposition of ethane manometrically and also by means of mass spectrometer analyses. The two methods were found to be in good agreement.

The Thermal Decomposition of C_2H_6 and C_2D_6. Relative Rates.—The speeds of decomposition of ethane and ethane-d_6 were measured manometrically at 613° both alone and in the presence of equal amounts of methane and methane-d_4. The results are given in Fig. 1 and summarized in Table I.

TABLE I

INITIAL RELATIVE RATES OF DECOMPOSITION OF C_2H_6 AND C_2D_6 AT 613°

	C_2H_6	C_2D_6
Pure hydrocarbon (100 mm.)	3.6	1
Hydrocarbon (100 mm.) with CH_4 (100 mm.)	4.0	1.3
Hydrocarbon (100 mm.) with CD_4 (100 mm.)	4.0	1.4

The Thermal Decomposition of C_2H_6 in Presence of CD_4.—We did three experiments on the decomposition of 50–50 mixtures of C_2H_6 and CD_4 at 600° in which we decomposed the ethane to the extent of approximately 2%, 5% and 6%. Mass spectrometric analyses of the products showed that in all three experiments there was detectable formation of CD_3H, C_2H_5D and HD but the amounts formed were only a few tenths of a per cent., slightly greater than our experimental error. In addition to these compounds there seemed also to be present a few tenths of a per cent. of CH_3D. We did not, therefore, do further work with these mixtures.

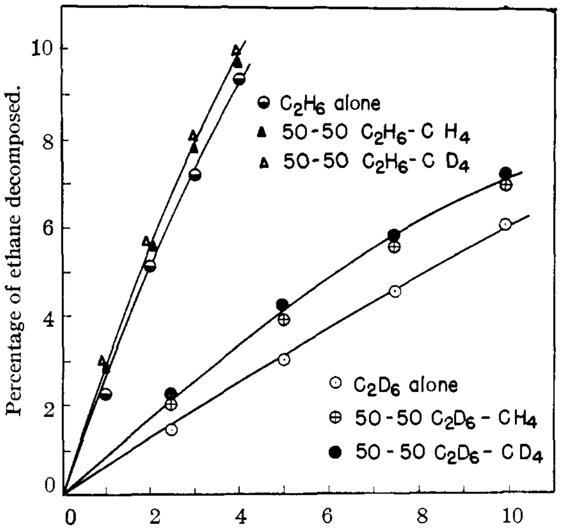

Fig. 1.—Thermal decomposition of C_2D_6 and C_2H_6 alone and in presence of CD_4 and CH_4 at 613°. Initial ethane pressure 100 ± 5 mm. in all experiments; manometric measurements.

The Thermal Decomposition of C_2D_6 in Presence of CH_4. Extent of Mixing.—In this case there was considerable mixing in contrast with C_2H_6 and CD_4, so that it is possible to follow accurately the changes in concentration of CH_3D, C_2D_5H and HD, with percentage decomposition of ethane-d_6. We found that the concentration of CH_3D was approximately directly proportional to the fraction of C_2D_6 decomposed. This same relation holds also for C_2D_5H and HD. We also found that the amount of CH_3D formed for a fixed fractional decomposition of the ethane was approximately independent of temperature. Our results are shown in Figs. 2, 3 and 4.

Extent of Mixing in Absence of C_2H_6 or C_2D_6.—Mixtures of CH_4 and CD_4 with or without NO show only very slight mixing under the conditions of our experiments. The same is true for mixtures of D_2 and CH_4.

TABLE II

MASS SPECTROMETRIC ANALYSIS OF CH_4–CD_4 AND D_2–CH_4 MIXTURES, HEATED AT 600° FOR 30 MIN. WITH AND WITHOUT NO

Mixture		Mole per cent.					
		D_2	HD	CH_4	CH_3D	CD_3H	CD_4
62 mm. CD_4	Init.	0	0	50	0	0.6	49.4
62 mm. CH_4	Final	0	0.5	49.8	0	.9	48.8
56 mm. CD_4	Init.	0	0	45.1	0	.6	44.5
56 mm. CH_4 12 mm. NO	Final	0	.01	44.9	.2	.7	44.2
75.6 mm. CH_4	Init.	10.0	0	90.0	0		
8.4 mm. D_2	Final	9.5	.5	90.0	.01		
81 mm. CH_4	Init.	9.4	0	84.6	0		
9 mm. D_2 5.5 mm. NO	Final	8.9	.5	84.6	.01		

The Rate of Decomposition of C_2H_6–NO Mixtures and C_2D_6–NO Mixtures.—In this section we describe a series of runs in which the rate of decomposition was followed manometrically. The inhibition of C_2D_6 with NO is similar to the C_2H_6 decomposition in the presence of NO (see Fig. 5) except that at maximum inhibition the rate is reduced to

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[9] We wish to thank Dr. Wall for making the necessary arrangements to transfer this sample and that of the CD_4.

[10] V. H. Dibeler and F. L. Mohler, *J. Research Natl. Bur. Standards*, **45**, 441 (1950); also private communication from the same authors.

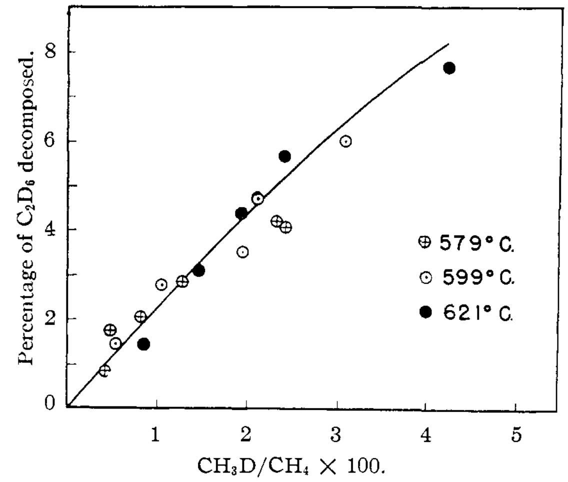

Fig. 2.—Thermal decomposition of 50–50 mixtures of C_2D_6 and CH_4: initial pressure of C_2D_6, 82 and 92 mm.; mass spectrometer measurements.

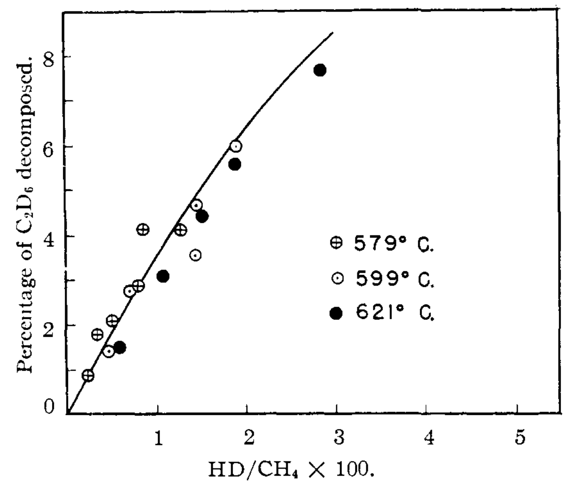

Fig. 3.—Thermal decomposition of 50–50 mixtures of C_2D_6 and CH_4. Initial pressures of C_2D_6 at 82 to 92 mm.; mass spectrometer measurements.

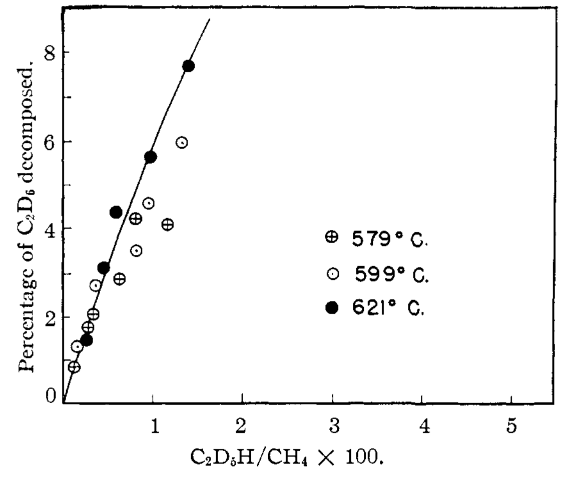

Fig. 4.—Thermal decomposition of 50–50 mixtures of C_2D_6 and CH_4: initial pressure of C_2D_6 82 to 92 mm.; mass spectrometer measurements.

18% and 8% of the uninhibited reaction for C_2H_6 and C_2D_6, respectively. We also ran a series of experiments (Fig. 5) in which we showed that CH_4 had no significant effect on the inhibition of C_2D_6 by NO.

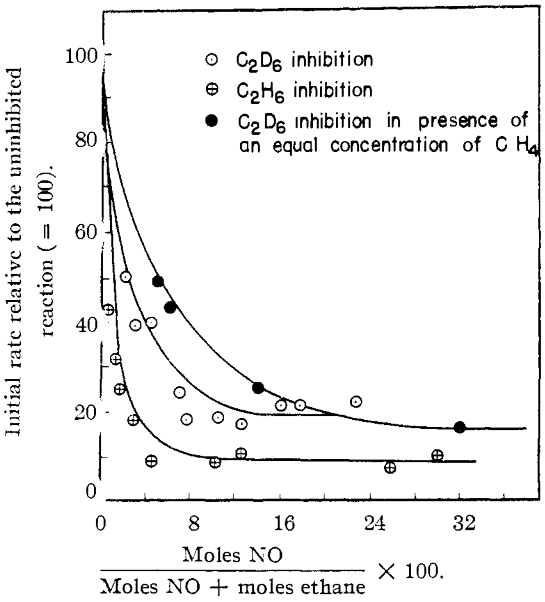

Fig. 5.—The nitric oxide inhibition of ethane-*d*₆ and ethane at 614° and initial pressure of 135 mm. The nitric oxide inhibition of 50–50 mixtures of C_2D_6 and CH_4 at 624° and initial ethane pressure in range of 65–90 mm., manometric measurements.

The Thermal Decomposition of C_2D_6–CH_4–NO Mixtures. —The decomposition of 50–50 mixtures of C_2D_6 and CH_4 was studied in presence of various amounts of NO. For the same fractional decomposition of the C_2D_6, it was found that the amount of CH_3D formed was independent of the concentration of NO. These results are shown graphically in Fig. 6.

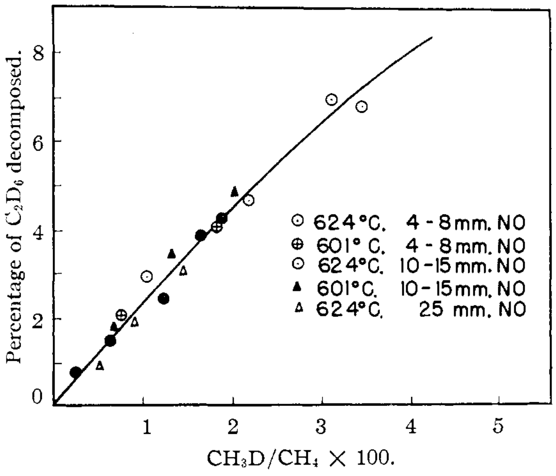

Fig. 6.—Thermal decomposition of 50–50 mixtures of C_2D_6 and CH_4 in presence of nitric oxide. Initial pressure of C_2D_6, 60–100 mm.; mass spectrometer measurements. The curve is that of the uninhibited reaction as given in Fig. 2.

We have expressed the results in another way (Fig. 7a) by plotting the ratio $CH_3D/CH_4 \times 100$ for an arbitrary fraction decomposition of ethane against percentage of nitric oxide present. If the decomposition occurs entirely through a chain mechanism, the points should all fall on a horizontal line whereas a quite different type of curve should be obtained for a composite type of decomposition. In Figs. 7b and 7c we give the result of a series of studies of the extent of formation of HD and C_2D_5H with the amount of inhibition. The results for HD are quite similar to those of CH_3D, but on the other hand the results for C_2D_5H indicate that except for rather small fractional decompositions, its concentration is not independent of the concentration of NO. We are conducting further experiments to elucidate this behavior.

Discussion and Summary

In this work we have tried to develop a general method which will give a quantitative indication of variations in the stationary state concentration of free radicals when an organic compound is thermally decomposed under different conditions. The method, in principle, consists of conducting a thermal decomposition in presence of a stable molecule and having either this molecule or the substrate fully deuterated. The extent of mixing, for a fixed fractional decomposition of the substrate, should be affected, if we do anything to alter the ratio of chain to non-chain decomposition.

One drawback, which is inherent in this method, makes it almost necessary to use the deuterated substrate and the hydrogenated indicator. This difficulty arises because[8,11] it is now fairly well established that the reaction

$$CH_3 + RH \longrightarrow CH_4 + R$$

proceeds several times faster than the reaction

$$CH_3 + RD \longrightarrow CH_3D + R$$

It would be quite difficult to make a quantitative analysis of the slight mixing that occurs when C_2H_6 is decomposed in presence of an equal quantity of CD_4, whereas considerable mixing occurs when C_2D_6 is decomposed in presence of CH_4.

While caution must be exercised in applying to the hydrogenated substrate, conclusions derived from a study of the deuterated substrate, we believe that the thermal decompositions of C_2H_6 and C_2D_6 are very similar, especially in their behavior to NO, and it seems reasonable to extend to the thermal decomposition of C_2H_6, our conclusion that the molecular mechanism of the C_2D_6 decomposition is insignificant.

Our selection of ethane as substrate has both advantages and drawbacks. The chief drawback is its high stability which greatly limits the choice of indicators; in fact, methane seemed to be the only satisfactory possibility. A second drawback is the rather pronounced back reaction which makes it necessary to confine measurements to the early part of the decomposition. On the other hand, the molecular mechanism for the ethane decomposition is very simple and should therefore be more marked than the molecular mechanisms for such decompositions as acetone, butane or dimethyl ether. The reasons for deciding between free radical mechanisms and molecular mechanisms are discussed in detail in a paper by Rice and Teller[12] published some years ago.

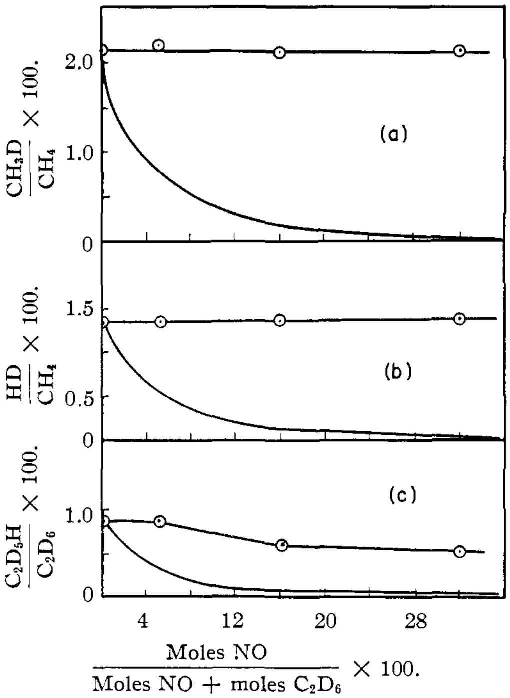

Fig. 7.—Thermal decomposition of 50–50 mixtures of C_2D_6 and CH_4 at constant fractional decomposition (4.5%) of C_2D_6: initial pressures of C_2D_6 75–100 mm.; temperature range 580° to 624°. The points were taken from the curves in Figs. 2 and 6. The lower curves in a, b and c were calculated from Fig. 5 on the assumption that the thermal decomposition of C_2D_6 consists of about 17% non-chain reaction.

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(11) W. Whittle and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 993 (1953).

(12) F. O. Rice and E. Teller, *ibid.*, **6**, 489 (1938).