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

The Thermal Decomposition of Ethane[1]

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It is shown that in the thermal decomposition of 50–50 mixtures of C_2H_6 and CD_4, the CD_3H/CD_4 ratio is approximately independent of the concentration of nitric oxide. In the thermal decomposition of 50–50 mixtures of C_2D_6 and CH_4, the D_2/CH_4 ratio is approximately independent of the concentration of nitric oxide, but the CD_3H/CH_4 ratio increases strongly with increasing concentration of nitric oxide. Mechanisms for these decompositions are proposed and discussed.

A recent paper by Rice and Varnerin[2] reported the thermal decomposition of ethane-d_6. We have studied the thermal decomposition of ethane and have also performed additional experiments on ethane-d_6 and are now able to report the CD_3H/CH_4 and the D_2/CH_4 ratios in the decomposition of 50–50 mixtures of C_2D_6 and CH_4 and the CD_3H/CD_4 ratio in the decomposition of 50–50 mixtures of C_2H_6 and CD_4. These experimental results, as well as some remarks on proposed mechanisms for these reactions form the subject matter of this paper.

Results

The apparatus, the mass spectrometer and the gases have been described previously.[2] The thermal decomposition of 50–50 mixtures of C_2H_6 and CD_4 were studied by decomposing them alone and in the presence of nitric oxide to different fractional decompositions at an initial ethane pressure of 80 mm. and at 582°. In Fig. 1 the CD_3H/CD_4 ratio is plotted against percentage of C_2H_6 decomposed. From these results it is seen that the amount of isotopic mixing, as measured by the CD_3H/CD_4 ratio, is approximately proportional to the percentage of ethane decomposed and is approximately independent of the presence of nitric oxide.

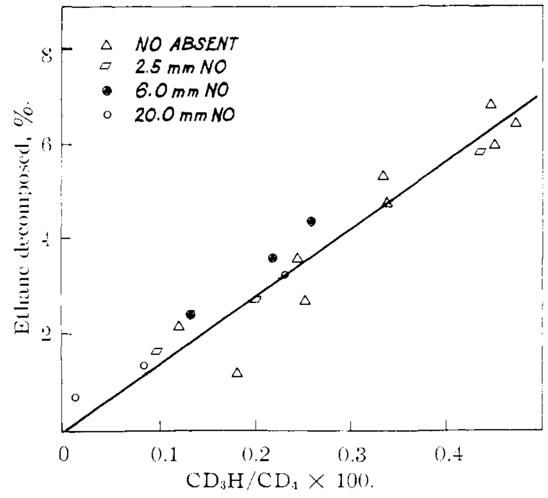

Fig. 1.—Thermal decomposition of equimolar mixtures of C_2H_6 and CD_4 alone and in presence of nitric oxide at 582° and an initial ethane pressure of 80 mm.; mass spectrometer measurements.

Reinvestigation of the thermal decomposition of 50–50 mixtures of C_2D_6 and CH_4 has been carried out. In addition to what was reported previously, the CD_3H/CH_4 and the D_2/CH_4 ratios can now be reported. These data are given in Figs. 2 and 3.

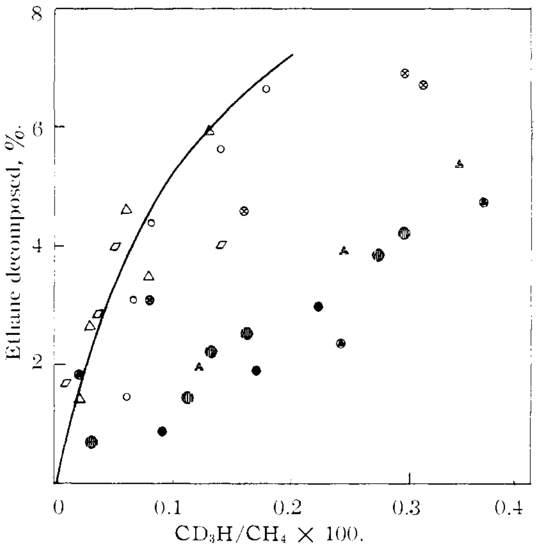

Fig. 2.—Thermal decomposition of C_2D_6 in presence of CH_4.

No. absent at		No. present	
△	600°	⊗	4.0 mm. at 624°
○	621°	◍	14.6 mm. at 624°
◇	579°	●	30.0 mm. at 624°
		●	9.0 mm. at 601°
		▲	6.7 mm. at 601°

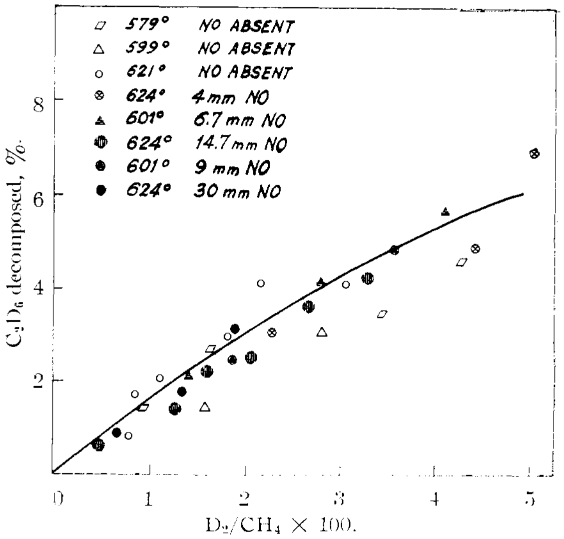

Fig. 3.—Thermal decomposition of mixtures of C_2D_6–CH_4 at an initial pressure of 80 mm. of C_2D_6.

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(1) This work was supported by the U. S. Air Force under Contract AF-18(600)-64 monitored by the Office of Scientific Research.

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

The D_2/CH_4 ratio, like the CH_3D/CH_4 and HD/CH_4 ratios reported previously, are approximately independent of the concentration of NO, but the CD_3H/CH_4 ratio increases sharply with increasing concentration of NO. This is not surprising since CD_3 radicals can be formed only by the initial split of C_2D_6.

A comparison of the proposed mechanism of the C_2H_6–CD_4 decomposition with the mechanism of the C_2D_6–CH_4 decomposition studied by Rice and Varnerin[2] follows.

The proposed reactions for the decomposition of C_2H_6 in the presence of CD_4 are given in Table I.

TABLE I

THERMAL DECOMPOSITIONS OF 50–50 MIXTURES OF C_2H_6 AND CD_4 REACTIONS

		k, mole^{-1} cc.$^{-1}$ sec.$^{-1}$
(1)	$C_2H_6 \longrightarrow CH_3 + CH_3$	
(2)	$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5$	7.3×10^{-16}
(3)	$CH_3 + CD_4 \longrightarrow CH_3D + CD_3$	7.3×10^{-17}
(4)	$CD_3 + C_2H_6 \longrightarrow CD_3H + C_2H_5$	7.3×10^{-16}
(5)	$C_2H_5 + CD_4 \longrightarrow C_2H_5D + CD_3$	7.3×10^{-16}
(6)	$C_2H_5 \longrightarrow C_2H_4 + H$	2.4×10^{4a}
(7)	$H + C_2H_6 \longrightarrow H_2 + C_2H_5$	1.0×10^{-13}
(8)	$H + CD_4 \longrightarrow HD + CD_3$	1.0×10^{-14}

[a] Sec.$^{-1}$.

The values of the rate constants in Table I were calculated from data in Steacie[3] and Trotman-Dickenson.[4] It was assumed that the activation energy of deuterium abstraction from a deuterated molecule is 1.7 kcal.[5] greater than for hydrogen abstraction from the corresponding ordinary molecule and that the A factors are the same. It was also assumed, since data are lacking, that ethyl and methyl radicals react with the same molecule at the same rate.

From this it can be seen that the reaction (2) is about 10 times as fast as reaction (3); reaction (5) is negligible compared to reaction (6); reaction (7) is about 10 times as fast as reaction (8). Since reactions (3), (5) and (8) are relatively inactive, the concentration of CD_3 must be low and one would not expect reaction (4) to produce CD_3H in any great quantity. This is borne out experimentally by the CD_3H/CD_4 ratio which is only 0.0035 for 5% decomposition of C_2H_6.

The reaction scheme proposed here may be considered as follows. Reaction (1) is the initial split of ethane into two methyl radicals. This is followed by a series of reactions between various radicals and C_2H_6 or CD_4. It should be noted that reaction of a radical with a molecule must always result in the generation of another radical which may or may not be the same as the original radical.

In our system we define a "chain radical reaction" as a member of a series of reactions initiated by a radical and ending with the same radical. Reaction (5) is an example of a chain radical reaction. A "non-chain radical reaction" is defined as one in which the initiating free radical is not subsequently regenerated. Reactions (2) and (3) are examples of this type of reaction. A reaction such as (4) is of a mixed type and may be classed either as a "chain radical reaction" or a "non-chain radical reaction" depending on which particular sequence is considered.

The three chains (see Table I) are considered as follows: Chain A formed by reactions (5) and (4) is insignificant. This is predicted from the values of the rate constants of reactions (5) and (6). Chain B, formed by reactions (6) and (7), is the most important one in this reaction. Again this is predicted by the values of the rate constants and is confirmed experimentally. Chain C, formed by reactions (6), (8) and (4), should be about one-tenth as effective as Chain B.

A similar mechanism for the C_2D_6–CH_4 decomposition studied by Rice and Varnerin[2] is shown in Table II, following the scheme of Table I. The rate constants are calculated in the same way. Here reaction (3) is of comparable importance to reaction (2); in a similar manner, reaction (8) is of importance to reaction (7). This means that reaction (4) should be more important in this scheme than in the case of the decomposition of C_2H_6. This is confirmed by the CH_3D/CH_4 ratio which is 0.025 for 5% decomposition of C_2D_6. This ratio is seven times as great as the corresponding ratio in the case of 5% decomposition of C_2H_6 in the presence of CD_4.

TABLE II

THERMAL DECOMPOSITION OF 50–50 MIXTURES OF C_2D_6 AND CH_4

		k, mole^{-1} cc.$^{-1}$ sec.$^{-1}$
(1)	$C_2D_6 \longrightarrow CD_3 + CD_3$	
(2)	$CD_3 + C_2D_6 \longrightarrow CD_4 + C_2D_5$	3.7×10^{-16}
(3)	$CD_3 + CH_4 \longrightarrow CD_3H + CH_3$	3.3×10^{-16}
(4)	$CH_3 + C_2D_6 \longrightarrow CH_3D + C_2D_5$	3.7×10^{-16}
(5)	$C_2D_5 + CH_4 \longrightarrow C_2D_5H + CH_3$	3.3×10^{-16}
(6)	$C_2D_5 \longrightarrow C_2D_4 + D$	2.4×10^{4a}
(7)	$D + C_2D_6 \longrightarrow D_2 + C_2D_5$	4.7×10^{-14}
(8)	$D + CH_4 \longrightarrow HD + CH_3$	4.1×10^{-14}

[a] Sec.$^{-1}$.

The results are expressed in a different manner in Table III which gives the number of moles of certain of the products formed for every 100 moles of ethane-d_6 which decomposes initially for various additions of nitric oxide. The amount of CH_3D formed remains essentially constant, the amount of C_2D_5H formed decreases and the amount of CD_3H formed increases appreciably as the NO concentra-

TABLE III

MOLES OF PRODUCTS PER 100 MOLES OF C_2D_6 DECOMPOSED IN PRESENCE OF VARIOUS ADDITIONS OF NITRIC OXIDE

NO, mm.	0	4.0	6.7	9.0	14.6	30
CH_3D	44	47	45	40	44	47
HD	34	34	29	28	32	27
D_2	87	83	72	63	75	64
C_2D_5H	18	19	16	11	11	6
CD_3H	2.1	3.9	6.0	6.3	6.5	7.8
$(CH_3D + D_2)$	131	130	117	103	119	111
CH_3D/CD_3H	25	12	7.6	6.3	6.9	6.0

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[3] E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y.

[4] A. F. Trotman-Dickenson, *Quart. Rev.*, **VII**, 210 (1953).

[5] J. R. McNesby, *et al.*, THIS JOURNAL, **76**, 823, 1416 (1954).

tion increases. The CD_3H concentration increases with increasing concentration of NO because CD_3H can be formed only in a non-chain radical reaction, it depends only on the initial split of the ethane-d_6 molecule and is independent of any chain. As the chain shortens with increasing concentration of NO, the initial split becomes more important and the concentration of CD_3H increases.

On the other hand, C_2D_5H is formed only in a chain-radical reaction. With addition of NO the chain becomes less important compared with the original split, and the concentration of C_2D_5H should fall. CH_3D can be formed either in a chain or non-chain radical reaction and its constancy with respect to increasing concentration of NO may be ascribed to a cancelling of two effects. The ($CH_3D + D_2$) row is a measure of the accuracy of the experimental data. For every molecule of C_2D_6 decomposing by a chain, a molecule of either D_2 or CH_3D is formed. Since the ($CH_3D + D_2$) values differ considerably from 100, our results are only semi-quantitative.[6]

As pointed out previously the CD_3H is a measure of the initial split of the C_2D_6. The CH_3D can be formed in either a "non-chain" or a "chain radical" reaction. If we neglect the CH_3D formed outside of the chain, the ratio of CH_3D to CD_3H (Table III) is essentially the length of the chain consisting of reactions (6), (8) and (4). The experimental results indicate that, as nitric oxide is added, the chain length decreases from 25 to about 6 links. As the chain length decreases the initial split of the C_2D_6 and the "non-chain radical" reactions become relatively more important than in the uninhibited reaction. This seems to be confirmed by the fact that the amount of CD_3H formed increases as the nitric oxide concentration increases.

These results support the previously published conclusion that the thermal decomposition of C_2H_6 or C_2D_6 is a chain reaction in which there is negligible direct molecular separation of H_2 or D_2.

Acknowledgment.—The authors wish to thank Dr. F. O. Rice who gave generously of his time and knowledge during the course of this work.

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[6] It was pointed out by the reviewer that the reactions designated as A, B and C are

A: $C_2D_6 + CH_4 \longrightarrow C_2D_5H + CH_3D$

B: $C_2D_6 \longrightarrow C_2D_4 + D_2$

C: $C_2D_6 + CH_4 \longrightarrow C_2D_4 + HD + CH_3D$

It is a consequence of this mechanism that

$$[C_2D_5H] = [CH_3D] - [HD]$$

It is seen from Table III that the data fit this relation at intermediate nitric oxide concentrations but deviate markedly at low and high concentrations.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Oxidation of Lower Paraffin Hydrocarbons. I. Room Temperature Reaction of Methane, Propane, *n*-Butane and Isobutane with Ozonized Oxygen[1]

BY CLARENCE C. SCHUBERT, S.J., AND ROBERT N. PEASE

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Reaction rates of ozonized oxygen (*ca.* 3 mole % O_3) with methane, propane, *n*-butane and isobutane were measured, *in situ*, in a temperature-controlled infrared absorption cell by observing the decrease of ozone concentration as measured by the absorption at 1055 cm.$^{-1}$. The activation energies calculated on the basis of a reaction first-order with respect to ozone were 14.9, 12.1, 11.1 and 10.3 kcal., respectively. The pre-exponential term for the methane–ozone reaction was found to be 7.2×10^{10}, for propane–ozone 3.1×10^{9}, for *n*-butane–ozone 8.2×10^{8} and for isobutane–ozone 4.4×10^{8} cc. mole^{-1} sec.$^{-1}$ estimated on the basis of a reaction rate $\propto [O_3][HC]$. The isobutane–ozone reaction was predominantly homogeneous; *n*-butane–ozone showed some acceleration in rate due to increased Pyrex surface, little dependence on sodium chloride surface. The main gaseous product of the isobutane–ozone reaction was *t*-butyl alcohol with smaller amounts of acetone and 1-carbon products approximately equal to molar amounts of acetone. A mechanism based on the postulation of a low lying triplet state of ozone is presented.

Relatively little work has been done on the kinetics of the action of ozone on saturated hydrocarbons. It was reported by Otto[2] in 1898 that ozone reacted with methane to yield aldehyde at temperatures as low as 15°. In 1922 Wheeler and Blair[3] observed that at 100° methane reacted with ozone at such speed that 53% of the introduced ozone disappeared within 2 minutes. Also in 1922 Elworthy[4] concluded that the reaction of methane with ozone gave promise as a means to produce methanol and formaldehyde. In 1928 Riesenfeld and Gurian[5] re-investigated this reaction.

Ethanol was reported[6] to result from the action of ozone on ethane and this reaction was noted to proceed with greater rapidity than the reaction of ozone with methane. Some patents[7] have been issued to cover the use of ozone as a stimulator for the combustion of gaseous, liquid or solid fuels.

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[2] M. M. Otto, *Ann. chim. phys.*, [VII] **13**, 109 (1898).

[3] T. S. Wheeler and E. W. Blair, *J. Chem. Soc. Ind.*, **41**, 303 (1922).

[4] R. T. Elworthy, *Trans. Roy. Soc. Can.*, [III] **16**, 93 (1922).

[5] E. H. Riesenfeld and D. Gurian, *Z. physik. Chem.*, **A139**, 169 (1928).

[6] W. A. Bone and J. Drugman, *Proc. Chem. Soc.*, **20**, 127 (1904).

[7] C. E. Thorpe, "Bibliography of Ozone Technology," Vol. 1, Armour Research Corp., Ill. Inst. of Tech., Tech Center, Chicago, 1954.