One gram of the sharply-melting (108–109°) product obtained by treating an acetic acid solution of 3,5-dibromoacetylmesitylene with an excess of bromine was pulverized in an agate mortar and shaken mechanically with 50 cc. of a 10% potassium hydroxide solution for twenty-four hours. Acidification of the reaction mixture (after washing with ether) gave a precipitate in insufficient amount for identification. Evaporation of the ether left a residue, from which the pentabromo ketone, melting at 112–113°, was isolated by extraction with hot alcohol. A small amount of a substance sparingly soluble in hot alcohol, and very soluble in benzene, was isolated but not identified.

Summary

It has been shown that bromine reacts in the absence of solvent with acetomesitylene to give a tribromomethyl ketone and a sharply-melting substance consisting of the same tribromomethyl ketone and the corresponding dibromomethyl ketone. Bromine in acetic acid was less efficient in halogenating the acetyl group since the chief product was the sharply-melting mixture of the dibromo- and tribromo-methyl ketones.

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The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IV. The Dehydrogenation of Paraffin Hydrocarbons and the Strength of the C–C Bond

BY F. O. RICE AND M. DENISE DOOLEY

The thermal decomposition of ethane has been studied recently in two papers,[1] and it has been concluded that the only reaction occurring to an appreciable extent is the simple dehydrogenation to C_2H_4; the reaction is homogeneous and unimolecular, with an activation energy of about 73 cal. It would seem from this that the decomposition of ethane can best be represented as the separation of molecular hydrogen from the ethane molecule with the formation of a double bond between the two carbon atoms to give ethylene. This view has received further support from the work of Pease,[2] who has shown that the formation of ethane from ethylene and hydrogen is a second order reaction with an energy of activation of 43,150 cal. The heat of the reaction $C_2H_4 + H_2 \longrightarrow C_2H_6$ at room temperature and constant pressure is 30,600 cal.[3] and at 600–700° and constant volume is 31,244 cal.[4] The activation energy of the reaction $C_2H_6 \longrightarrow C_2H_4 + H_2$ is therefore $43{,}150 + 31{,}244 = 74{,}394$ cal., a figure which is in excellent agreement with the experimental value of 73,170 cal. obtained by Marek and McCluer.[1]

(1) Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); Marek and McCluer, *ibid.*, **23**, 878 (1931).
(2) Pease, THIS JOURNAL, **54**, 1878 (1932).
(3) Von Wartenberg and Krause, *Z. physik. Chem.*, **151**, 105 (1930).
(4) Pease and Durgan, THIS JOURNAL, **50**, 2715 (1928).

One might expect from this that the dehydrogenation, not only of ethane but also of its homologs, can best be represented as the separation of molecular hydrogen with the formation of the corresponding olefin hydrocarbon. Now if this simple process really takes place, it seems reasonable to suppose that there would be some fairly obvious relation between the structure of a hydrocarbon and the extent of the dehydrogenation process. The experimental results for several hydrocarbons are given in Fig. 1 (heavy line);[5] an inspection of these shows that the structure of the hydrocarbon gives no clue as to the extent to which dehydrogenation takes place; thus propane gives 23% hydrogen in the products but *n*-butane only 4.5%; isobutane gives 26.4% which cannot be due to a tertiary hydrogen atom because 2,3-dimethylbutene gives only 3% hydrogen.

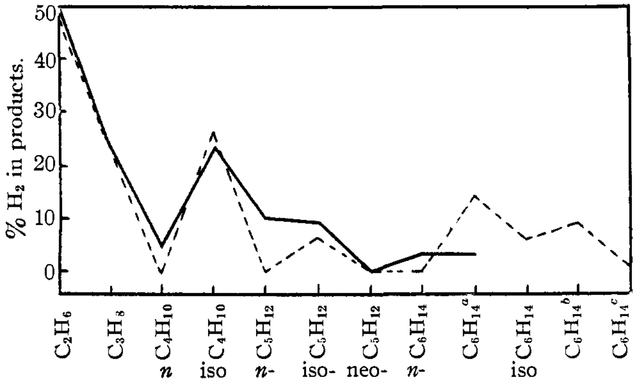

Fig. 1.—Observed (—) and calculated (- - -) hydrogen production in the thermal decomposition of hydrocarbons. [a] 2,3-Dimethylbutane. [b] 2,2-Dimethylbutane. [c] 3-Ethylpentane.

When, however, we consider the decomposition from the standpoint of free radicals,[6] the agreement is much better; the calculated results are shown in Fig. 1 (dotted line).

It occurred to us that it is possible to make an experimental test of these two mechanisms by decomposing ethane according to a method already described[7] and testing for the presence of free radicals by the Paneth effect[8] on metallic mirrors. Ethylene[9] has no effect on a metallic mirror when heated under these conditions, and we confirmed the original observation of Paneth and Hofeditz[8] that hydrogen also has no effect. Therefore, if ethane decomposes according to the equation $C_2H_6 \longrightarrow C_2H_4 + H_2$, there should be no removal of a metallic mirror; whereas, if it decomposes according to the equation $C_2H_6 \longrightarrow 2CH_3$, mirrors should be readily removed.

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(5) Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933).

(6) Rice, This Journal, **53**, 1959 (1931); **55**, 3035 (1933).

(7) Rice, Evering and Johnston, *ibid.*, **54**, 3529 (1932).

(8) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(9) Fred R. Whaley, Ph.D. Thesis, **1932**, Johns Hopkins University.

A preliminary test with ordinary commercial ethane (90%) showed rapid removal in the range 850–950°. However, in order to determine that the effect was not due to small amounts of impurities (such as propane), we prepared a sample of ethane by the Grignard reaction, using methylmagnesium bromide, and removed ether and other impurities by passing through a trap at −80° and distilling through a vacuum jacketed column. This sample and the commercial sample gave identical results. We concluded therefore that the reaction $C_2H_6 \longrightarrow 2CH_3$ takes place at any rate to some extent in the range 850–950°.

Our next step was to measure the activation energy of this reaction[10] by depositing standard mirrors of antimony on the walls of the tube at different distances from the furnace. In this manner we obtained a relative measure of the concentration of radicals at the end of the furnace at measured furnace temperatures. We performed a number of experiments using in each case commercial ethane which had been distilled through a vacuum jacketed column. In one series of experiments at 960 and 906° using a quartz tube 1.3 cm. in diameter and a furnace 15 cm. long we obtained the following results

Dist. from end of furnace, cm.	2.5	2.1	1.5	1.0	0.7
Ratio t_{906}/t_{960}	3.14	3.31	3.73	3.88	4.08
Activation energy	61,600	64,500	71,000	73,000	76,000

The ratio t_{906}/t_{960} is the ratio of the times of disappearance of two standard mirrors for these two furnace temperatures; the extrapolated value for the end of the furnace is 4.44, which corresponds to an activation energy of 80,000 cal. The mean value of three such experiments with ethane is 79,500 ± 3000 cal. In order to test the apparatus we performed a similar experiment using acetone at furnace temperatures 742 and 795° and obtained an activation energy of 69,000 cal. which is also in good agreement with a previous result.

Summary

We have shown that when ethane is heated in the range 850–950° free radicals are present. Furthermore, we have shown that the activation energy of the dissociation of ethane into methyl groups is very close to the measured activation energy of ethane. Accordingly, either the formation of ethylene and hydrogen from ethane goes through a free radical mechanism, or the free radical mechanism and a simple separation of hydrogen occur simultaneously. The value 79,500 cal. for the dissociation of ethane into two methyl groups plus the average energy (about 5000 cal.) gives an upper limit for the strength of the C–C bond.

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[10] See Ref. 7, p. 3540.