

to the single easily applied condition that the correct activation energy was obtained. If no assignment could be found which satisfied this condition and gave satisfactory maintenance of the rate, it would be necessary to abandon the mechanism which has been suggested. It seems likely, however, that there would prove to be an ample margin of safety.

It is difficult to know what should be said about the induction period. The view that it represents the formation of steady state concentrations of the intermediate products became untenable when these concentrations were shown to be less than 0.1 mm. It can scarcely be caused by adsorption on the walls of the initial amounts of hydrogen produced, since in that case it would have become much more prominent in the packed vessel; actually, it was not observed at all. For a reaction of this character, it is almost unthinkable that any impurity could be responsible for an induction period. It would appear probable that the explanation lies in some peculiarity of the experimental arrangements, and that there is really no induction period at all.

Summary

The thermal decomposition of methane has been studied in quartz bulbs at 700–850°. The initial reaction is homogeneous and kinetically first order. The primary process is probably the unimolecular reaction $\text{CH}_4 = \text{CH}_2 + \text{H}_2$, with a rate constant $5 \times 10^{11} e^{-79385/RT}$; the observed rate constant is twice this, since the next step in the reaction is considered to be $\text{CH}_2 + \text{CH}_4 = \text{C}_2\text{H}_6$. The rate of methane decomposition is very greatly retarded by hydrogen; when this is present in sufficient quantity the reaction rate becomes proportional to $[\text{CH}_4]^2/[\text{H}_2]^3$. This result, together with the more complex hydrogen dependence of the intermediate stages, is fully accounted for by supposing that the ethane dehydrogenates in successive steps to ethylene, acetylene and finally carbon, and that all the reactions involved in the mechanism are reversible.

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NOTE

The Strength of Semicarbazide—and a Correction

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Bartlett¹ gives a value of 3.68 at 25° and $\mu = 0.079$ for the uncorrected acid dissociation constant (pK_A) of semicarbazide cation. This prompts me to call attention to the value of 3.65 for the same constant, obtained here² by Dr. Marshall R. Sprinkle by a similar method at 26° and at ionic strengths between 0.05 and 0.046. These two independent determinations seem to settle the question.

¹ Bartlett, *THIS JOURNAL*, **54**, 2857 (1932).

² Hall, *ibid.*, **52**, 5124 (1930).

I must also note a regrettable error in my own recalculation² of Wood's value, which should read 3.07 at 25° instead of 3.67. This calculation is based on the temperature coefficients determined in this Laboratory.³

³ Hall and Sprinkle, *THIS JOURNAL*, **54**, 3469 (1932).

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ANALYSIS OF SMALL QUANTITIES OF VOLATILE MATERIAL BY DETERMINATION OF THE VAPOR PRESSURE AND MOLECULAR WEIGHT DURING DISTILLATION

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The distillation analysis of liquid petroleum products is of importance as a criterion of their technical properties. Conclusions as to the adaptability of a motor to changes of load, the determination of the necessary preheating of the main air, of the cooling water temperature, etc., may be drawn from the behavior of a benzine during distillation.¹

The A. S. T. M. method² specifies the use of 100 cc. of liquid in accordance with the original method of Engler-Ubbelohde.³ In the course of our catalytic work on a laboratory scale, however, it often became necessary to analyze such reaction products, available in very small quantity. Yields of liquid products of 12–14 cc. usually result from 100 liters of water gas in a gasoline synthesis with cobalt catalysts by the Fischer-Tropsch method.⁴ Small amounts of hydrocarbons are often produced in high pressure hydrogenations, and their behavior during distillation is of interest.

The distillation analysis of small quantities of material has been the subject of numerous researches, so a survey of the subject is unnecessary. The procedures of Gawalowski,⁵ Gross and Wright,⁶ and those of Pregl⁷ are microdistillation methods. In all of them the apparatus has been designed for the handling of small amounts of material. Berl and Althoff⁸ have designed such an apparatus, using a packed tower and a dephlegmator at a definite temperature; this apparatus works satisfactorily with 8–10 cc.

¹ Wa. Ostwald, *Glückauf*, **61**, 550 (1925).

² A. S. T. M. Ser. design, D. 86-27; Bureau of Mines, *Tech. Papers* 323, b. p. 49.

³ Ubbelohde, *Mitt. a. d. Materialprüf.-Amt. Berlin*, **25**, 261 (1907).

⁴ F. Fischer and H. Tropsch, *Ber.*, **59**, 830 (1926); literature by Fischer, *Brennstoff-Chemie*, **11**, 489 (1930).

⁵ Gawalowski, *Z. anal. Chem.*, **49**, 744 (1910).

⁶ P. Gross and A. H. Wright, *J. Ind. Eng. Chem.*, **13**, 701 (1921).

⁷ F. Pregl, "Die quantitative organische Mikroanalyse," Julius Springer, Berlin, 1930, p. 220.

⁸ E. Berl and F. W. Althoff, *Die Chem. Fabrik*, **3**, 220 (1930).