micrograms of bromide in 0.1 cc. of solution, 1 to 4 micrograms in 1.0 cc., and 3–18 micrograms in 10 cc. Chlorides do not interfere, while iodides may be removed with nitrite and acid. Reducing agents must be removed or oxidized.

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[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

The Role of Methyl and Methylene Radicals in the Decomposition of Methane[1]

BY LOUIS S. KASSEL[2]

The rate of thermal decomposition of methane in the absence of appreciable hydrogen is controlled by a unimolecular process with an activation energy of 79,000 cal. When hydrogen is present the reaction is very strongly retarded, and with sufficient hydrogen the rate can be represented as $k(CH_4)^2/(H_2)^3$.[3] These results were shown to agree well with the mechanism

$$\begin{aligned} CH_4 &= CH_2 + H_2 && (1)\\ CH_2 + CH_4 &= C_2H_6 && (2)\\ C_2H_6 &= C_2H_4 + H_2 && (3)\\ C_2H_4 &= C_2H_2 + H_2 && (4)\\ C_2H_2 &= 2C + H_2 && (5) \end{aligned}$$

which gives the rate equation

$$-\,d(CH_4)/dt = 2\,\frac{k_1k_2k_3k_4k_5(CH_4)^2 - r_1r_2r_3r_4r_5(H_2)^4}{r_1r_2r_3r_4(H_2)^3 + r_1r_2r_3k_5(H_2)^2 + r_1(r_2 + r_3)k_4k_5(H_2) + k_2k_3k_4k_5(CH_4)}$$

where k and r refer to the forward and reverse reaction, respectively. Important support for this scheme was furnished by the experiments of Storch,[4] which definitely established the sequence of products $C_2H_6 \longrightarrow C_2H_4 \longrightarrow C_2H_2 \longrightarrow C$. Subsequently Belchetz[5] reported confirmation of the production of methylene by flowing methane at 0.1 mm. pressure past a heated platinum filament and then over iodine or tellurium mirrors at a distance of 3 mm. from the filament. With tellurium mirrors a product was obtained which reacted with bromine to give CH_2Br_2; this product could not have been $Te_2(CH_3)_2$, which would have been formed from methyl groups, but could have been $TeCH_2$ or a polymer thereof. With iodine mirrors, CH_2I_2 was formed, and at filament temperatures above 1423°K., HI as well. These experiments thus seemed to indicate that the primary decomposition of methane produces methylene and no atomic hydrogen, and hence must be

$$CH_4 = CH_2 + H_2$$

These results and this conclusion have been attacked recently by Rice and Dooley,[6] who passed methane through a heated quartz tube and over mirrors of tellurium or antimony at a minimum distance of 1 cm. from the furnace. With tellurium mirrors they obtained $Te_2(CH_3)_2$, and no trace of the bright red, nonvolatile $(TeCH_2)_x$ which Rice and Glasebrook[7] found when similar experiments were made with diazomethane at furnace temperatures up to 600°. Rice and Dooley conclude that since the tellurium product of Belchetz was obviously not the $(TeCH_2)_x$ of Rice and Glasebrook, it was not any form of $TeCH_2$, and suggest that it was sublimed Te. Ignoring the CH_2Br_2 produced from Belchetz's product, and the CH_2I_2 he obtained with iodine mirrors, they reject reaction (1) and propose $CH_4 = CH_3 + H$ in spite of their own failure to find any atomic hydrogen. Further unpublished work of Rice[8] casts doubt upon the correctness of Belchetz's analytical results; this work did not include a repetition of Belchetz's experiments.

It is not the purpose of this discussion to reconcile these conflicting experiments, though it may be in order to point out that the temperature gradient in the arrangement of Belchetz was far steeper than that of Rice and Glasebrook and that this, or some other technical difference, may have led to different polymers of $TeCH_2$ in the two cases. Whatever radicals may be detectable, however, it does not appear possible to account for the observed kinetics of methane decomposition by a mechanism which involves methyl radicals. Attention is confined

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[3] Kassel, THIS JOURNAL, **54**, 3949 (1932).

[4] Storch, *ibid.*, **54**, 4188 (1932).

[5] Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934).

[6] Rice and Dooley, THIS JOURNAL, **56**, 2747 (1934).

[7] Rice and Glasebrook, *ibid.*, **56**, 2381 (1934).

[8] Rice, private communication.

here to the initial stages, and a mechanism is sought which will give the over-all reaction

$$2CH_4 = C_2H_6 + H_2$$

with a *first order* rate constant of

$$k = 10^{12}\, e^{-79,000/RT} \text{ sec.}^{-1}$$

Possible elementary reactions are

$$CH_4 = CH_3 + H \qquad (1)$$
$$CH_3 + CH_4 = C_2H_6 + H \qquad (2)$$
$$H + CH_4 = CH_3 + H_2 \qquad (3)$$
$$H + H = H_2 \qquad (4)$$
$$H + CH_3 = CH_4 \qquad (5)$$
$$CH_3 + CH_3 = C_2H_6 \qquad (6)$$

If the chains are long, one readily finds

$$(CH_3) = \sqrt{\frac{k_1k_3^2(CH_4)}{k_2^2k_4 + k_2k_3k_5 + k_3^2k_6}}$$

This will give a reaction of the three-halves order unless the denominator contains a hidden factor (CH_4), as would be the case if reactions (4), (5) and (6) occurred at triple collisions. We cannot permit such a factor in k_5, since it would then be required in k_1 also, and the order could not be reduced. Rice cannot permit it in k_6 without abandoning the mechanism of Rice and Herzfeld[9] for the acetaldehyde decomposition, as well as their interpretation of the low pressure decomposition of methyl ether; it is unlikely on general grounds also that a third body would be required in this case. Reaction (4) will certainly contain the desired hidden factor; it is thus necessary to have (4) as the main chain breaking reaction and hence to have

$$k_2^2k_4 \gg k_2k_3k_5 \qquad k_2^2k_4 \gg k_3^2k_6$$

Now at 1 cm. pressure, where the reaction is still first order, we may feel sure that

$$k_4/k_5 < 10^{-4} \qquad k_4/k_6 < 10^{-4}$$

even if (5) and (6) have an activation energy of 8000 cal. and hence occur at 1 collision in 100. This requires

$$k_2 \gg 10^4k_3$$

furthermore

$$(H) = (k_2/k_3)(CH_3)$$

and hence

$$(H) \gg 10^4(CH_3)$$

This result conflicts hopelessly with Rice and Dooley's experiments in which methyl groups could be detected, but no atomic hydrogen; it does not seem possible that wall recombination of the atomic hydrogen could overcome so tremendous a factor. Moreover, it is highly improbable that (2) would be even as fast as (3). The postulate of long chains is thus extremely unsatisfactory.

If there are no chains, the rate will be either $k_1(CH_4)$ or twice this. Rice and Dooley find an activation energy of 100,000 cal. for k_1, and it is unlikely on thermochemical grounds that the value would be less than this figure. If the activation energy for methane decomposition is really this large, however, the author must have made the fantastic error of 32° in measuring a temperature interval of 105°; furthermore, extrapolation of the author's rates to 1500°, using his own activation energy, gives $k = 160$ sec.$^{-1}$ against de Rudder and Biedermann's value[10] of 50 sec.$^{-1}$; extrapolation with $E = 100,000$ cal. would give $k = 15,000$ sec.$^{-1}$. Finally, the rate would be $k_1 = 3 \times 10^{16}\, e^{-100,000/RT}$; a rate this large could not possibly be maintained at a pressure of 1 cm., and the order would again be increased due to a deficiency of activating collisions.

The case of short chains leads to cumbersome equations, which will not be given here; it is not difficult to see, however, that there is no safe passage between the horns of the dilemma in this way.

One cannot prove the correctness of a complex mechanism by its agreement with kinetic data, but one can prove its incorrectness by its disagreement. The apparent conclusion is that while the author's methylene mechanism is not necessarily right, Rice and Dooley's methyl radicals certainly have no relation to the main course of methane decomposition. Since there seems to be no third possibility, one is perhaps entitled to believe that the methylene mechanism is correct, and that further study of the experiments with tellurium mirrors will yield an interpretation of these results in harmony with that mechanism.

Summary

The experimental kinetics of methane decomposition cannot be explained by any mechanism which involves methyl radicals. The kinetics can be explained by the author's previously published methylene mechanism. It seems unwise to follow Rice and Dooley in discarding this mechanism on the basis of imperfectly understood and experimentally uncertain results obtained with tellurium mirrors.

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[9] Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

[10] De Rudder and Biedermann, *Bull. soc. chim.*, **47**, 704 (1930).