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## The Thermal Decomposition of Ethane

Remarks About a Paper by E. W. R. Steacie and N. W. F. Phillips

(J. Chem. Phys. 4, 461 (1936))

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On account of the experimental value of the reaction  $D + C_2H_6$  according to Steacie and Phillips the radical chain mechanism in the decomposition of ethane by F. O. Rice is anew discussed. It results that even now this theory does not agree with the experiment.

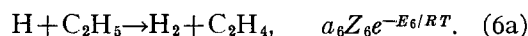
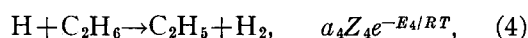
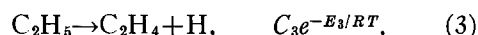
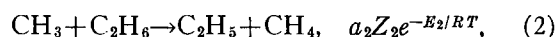
THE radical chain theory of the thermal decomposition advanced by F. O. Rice<sup>1</sup> was tested by Patat and Sachsse<sup>2</sup> by measuring the radical concentration during decomposition. Especially in the case of ethane Sachsse<sup>3</sup> found a H atom concentration three powers of ten smaller than that required by the calculation of Rice and Herzfeld.

Recently Steacie and Phillips<sup>4</sup> have studied the reaction of D atoms produced by an electrical discharge with ethane according to the equation:  $D + C_2H_6 = HD + C_2H_5$ . They found for this reaction at room temperature a heat of activation of 6300 cal. with a steric factor of 0.1. For the reaction of H atoms with ethane they assume a value of equal magnitude. With this value they revise the calculation of Rice and Herzfeld who had used 17,000 cal. for the said reaction. They conclude that on the account of the new value the H atom concentration required by the chain mechanism is now considerably smaller, and they say that it agrees almost exactly with our experimental value. The first part of this sentence is doubtless right, but the conclusion of the exact conformity is based on a misunderstanding.<sup>5</sup>

Therefore using the new value of Steacie and Phillips in the following we shall calculate once

more as accurately as possible the radical concentration required by the chain mechanism, while discussing various assumptions, and shall compare the result with experiment. For such an exact numerical comparison ethane appears to be the most adequate example. For firstly, its chain mechanism is especially obvious and simple, and in the second place the chain carrier itself, the H atom, can be determined directly by the parahydrogen method; thus the number of required assumptions is less here than in other decomposition processes.

According to the assumptions of Rice and Herzfeld the decomposition of ethane proceeds by the following steps:



Here  $C$  signifies the constants of the monomolecular decomposition processes which are independent of temperature,  $Z$  the collision numbers, and  $a$  the corresponding steric factors. For the stationary radical concentrations the authors arrive at:

$$[H] = (k_1 k_8 / 2 K_4 K_6)^{1/2}, \quad [CH_3] = K_1 / K_3, \\ [C_2H_5] = [C_2H_6] \cdot (K_1 K_4 / 2 k_6 k_3)^{1/2}.$$

In the Table I the H atom concentration and the velocity constant are calculated and com-

<sup>1</sup> F. O. Rice, J. Am. Chem. Soc. **53** (1931); F. O. Rice, K. F. Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934).

<sup>2</sup> F. Patat, H. Sachsse, Nachr. Ges. Wiss. Goettingen **1**, 41 (1934); Zeits. f. physik. Chemie **B31**, 105 (1935).

<sup>3</sup> H. Sachsse, Zeits. f. physik. Chemie **B31**, 79 (1935).

<sup>4</sup> Steacie and Phillips, J. Chem. Phys. **4**, 461 (1936).

<sup>5</sup> In their calculation the authors apparently use the figures of my Table 3, Zeits. f. physik. Chemie **31**, 85 (1935). But these figures have not been calculated on the basis of the Rice-Herzfeld mechanism. They only are to be used with a mechanism meeting the following condition:  $H = \text{const. } 1/k_4$ . This is not the case with the mechanism of F. O. Rice and it would be difficult to suggest such a mechanism for the decomposition of ethane which at the same time gives the correct order for the decomposition.

TABLE I. *H* atom concentration and velocity of reaction calculated according to the radical chain theory supposing different values of the fractional reactions.

| $C_1$       | $E_1$ | $C_3$       | $E_3$ | $a_4$ | $E_4$ | $a_6$      | $E_6$ | $[H] \cdot 10^{12}$<br>calc.        | log $k$ calc.                        |
|-------------|-------|-------------|-------|-------|-------|------------|-------|-------------------------------------|--------------------------------------|
| $10^{14}$   | 80    | $10^{14}$   | 49    | 0.1   | 6.3   | 0.1        | 8     | 320                                 | 14 -63500/2.3RT                      |
| $10^{14}$   | 80    | $10^{14}$   | 49    | 0.1   | 6.3   | $10^{-3*}$ | 0     | 310                                 | 15 -67500/2.3RT                      |
| $10^{14}$   | 71    | $10^{14}$   | 49    | 0.1   | 6.3   | 0.1        | 8     | 4350                                | 14 -58500/2.3RT                      |
| $10^{13.5}$ | 80    | $10^{13.5}$ | 49    | 0.1   | 6.3   | 0.1        | 8     | 103                                 | 13.5-63500/2.3RT                     |
|             |       |             |       |       |       |            |       | $[H] \cdot 10^{12}$ observed<br>6.3 | log $k$ observed<br>14.5-69800/2.3RT |

\* Ternary collision.

pared with the experimental values using different data for the several partial reactions. For the collision diameter of  $C_2H_6$  and  $C_2H_5$  there has been used 3.3A, for that of H 2.3A. The main uncertainty is caused by the constants  $C_1$  and  $C_3$  for which Rice and Herzfeld give the value  $10^{14}$ . Taking this uncertainty into account in one calculation there has been inserted  $10^{13.5}$  for these two constants to give a more favorable chance for the chain mechanism. In the assumptions of Rice the values of  $E_1$  and  $E_3$  are already relatively high, though in fact they are rather lower than higher. Particularly for the dissociation energy of ethane besides the value of Rice there is also to be considered the lower value of 71,000 cal. resulting from the general strength of the C—C linking. In consequence of the determination of Steacie and Phillips there would probably be not much change of  $a_4$  and  $E_4$ , also  $a_6$  and  $E_6$  hardly cause uncertainty, this reaction *per se* already being supposed to be rapid. As may be noted, it remains the same whether one supposes a triple collision or a rapid bimolecular reaction causing the chain rupture.

As may be noted, there is still a substantial discrepancy between experiment and theory even if all suppositions for the chain mechanism are as favorable as possible. Also the activation energies show a discrepancy far beyond the limits of error compared with my determination of 69,800 cal. or with that of Mareck and

McCluer<sup>6</sup> of 73,000 cal. Smaller values of  $C_1$  and  $C_3$  give no agreement at all with the experimental C-factor of 14.5 (H.S.) or 15.2 (Mareck and McCluer).

Finally we have still to discuss whether the decomposition is caused by chain reactions even if one rejects the mechanism of Rice and Herzfeld. The most obvious assumption already discussed by ourselves is the recombination of the H atoms at the wall. As is easily seen, this mechanism gives the 2nd to the 3rd order of ethane decomposition while Mareck and McCluer as well as myself most definitely found the first order.

Thus, it seems not to be possible to propose any chain mechanism which agrees reasonably with experiment. Now as formerly it is not denied that a certain percentage of all the decomposing molecules also form radicals, and on account of the new value of Steacie and Phillips just this part is increased, but even now it is only a small fraction of all the reacting molecules. Therefore the chain mechanism seems to be still inadequate to explain the whole process of the decomposition of ethane. We do not want to discuss other decomposition processes in detail. It would lead to the same result though the calculations would probably contain more uncertainties, and, there is no evident reason to assume a behavior substantially different from that of ethane in the decomposition of acetaldehyd, acetone, etc.

<sup>6</sup> Ind. Eng. Chem. **23**, 878 (1931).