INDUCTION PERIODS IN PYROLYTIC REACTIONS

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The Rice-Herzfeld mechanism for ethane decomposition is re-examined and is shown to lead to the expectation of short induction periods of observable length at about 850° K, caused by a slow approach to the stationary state. A discussion is given of the use of induction periods for estimating the velocities of reactions where direct observation is difficult, and examples of this use are given.

It is well established that induction periods may be observed in gaseous reactions which proceed by consecutive or by radical-chain reactions, if the process is autocatalytic, or in the presence of inhibitors respectively. It is generally assumed that the steady state is so rapidly established in a pyrolysis of the radical-chain type that induction periods are not expected to arise from this cause. The purpose of this paper is to question whether this assumption is always true.

Burnett[1] has shown that non-stationary phases of reaction may be observed in photopolymerization reactions, but until recently there has been little reliable experimental evidence that induction periods, arising as a result of approach towards the steady state, could be observed in pyrolytic reactions. For example, it has been pointed out[2] that those reported by Allen[3] in the slow pyrolysis of acetone, were probably caused by condensation. It is possible that the (somewhat irreproducible) induction periods reported by Pease and Morton,[4] and by Kuchler,[5] in the thermal decompositions of cycloparaffins may be due to a slow build up towards the steady state in each case. However, a considerable amount of recent work[6] upon the decompositions of chlorohydrocarbons has produced convincing evidence for the existence of such induction periods. The method used in the preceding paper for calculating the length of the induction period (graphical integration) may be applied quite generally to a chain reaction scheme, provided that the rates of the elementary steps are known. This has been done in the ethane decomposition and leads to the conclusion that induction periods may be expected in this reaction.

From inhibition studies,[7, 8, 9] ethane pyrolysis is clearly a chain reaction, and the results of Partington[10] show that competing non-chain processes do not amount to more than a few per cent. of the total reaction. Two excellent recent reviews[11, 12] of the reaction are available and it seems likely that the decomposition proceeds by the chain mechanism first proposed by Rice and Herzfeld:[13]

$$C_2H_6 \xrightarrow{k_1} 2CH_3 \qquad (1)$$

$$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5 \qquad (2)$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H \qquad (3)$$

$$H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5 \qquad (4)$$

$$H + C_2H_5 \xrightarrow{k_5} \text{products} \qquad (5)$$

Of the various experimental investigations of the uninhibited reaction, probably the most reliable are those carried out in static apparatus by Sachsse[14] and by Steacie and Shane,[15] who agree that

$$k = 10^{14} \exp(-69700/RT) \text{ sec}^{-1}.$$

From consideration of Partington's results,[10] this value for k may be set equal to that of the chain part of the decomposition and the experimental result follows from the chain mechanism if the individual steps have these rate constants in the region of 900° K: $k_1 = 10^{14} \exp(-87900/RT)$ sec^{-1}, $k_2 = 10^6 \exp(-9500/RT)$ l. mole^{-1} sec^{-1}, $k_3 = 10^{14} \exp(-42000/RT)$ sec^{-1}, $k_4 = 10^8 \exp(-9500/RT)$ l. mole^{-1} sec^{-1}, $k_5 = 10^8$ l. mole^{-1} sec^{-1}.[16] This mechanism, when analyzed in the usual steady state manner, predicts first-order kinetics with $k = \sqrt{(k_1k_3k_4/k_5)^{\frac{1}{2}}}$, and it can be reconciled with the results of Staveley [8] and Hobbs and Hinshelwood [9] on the inhibition of the decomposition by nitric oxide.

It is not true, however, that steady state conditions are established in a time which is negligible in comparison with that required for (say) 12½ % completion of reaction towards the $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ equilibrium—used by Steacie and Shane [15] for the calculation of rate constants. Graphical integration of steps 1-5 gives the following results:—

temp., °K	initial pressure, mm	induction period, sec[17]
850	200	27·3
900	200	8·3
900	600	3·9

Since the rate of reaction is equal to $k_3[C_2H_5]$, the induction period (defined in the preceding paper) may be calculated as

$$I = t_1 - \frac{\int_0^{t_1} [C_2H_5]\mathrm{d}t}{[C_2H_5]_\infty},$$

where $[C_2H_5]_\infty$ is the value of $[C_2H_5]$ at t_1, a time just great enough for the steady state to have been reached. I is conveniently obtained from a graph of $[C_2H_5]$ against time. In order to facilitate practical appreciation of the application and results of the calculation, one example of the variation of all the radical concentrations with time is shown in fig. 1, where the results are plotted in logarithmic fashion because of the enormous range of the variables. We may conclude therefore that a reasonable assignment of chain steps leads to the result that induction periods of observable length are expected in the pyrolysis of ethane. As yet, no investigator has described the existence of such induction periods, although possible evidence for their occurrence may be obtained from the results of Steacie and Shane.[15] These authors report that k falls as reaction proceeds and quote mean rate constants at 880° K, calculated from "initial" rates and the times for

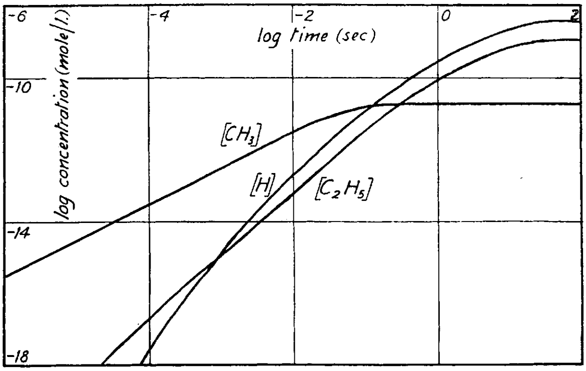

FIG. 1.—Graph of log concentration against log time for the methyl and ethyl radicals and hydrogen atoms in the approach to the steady state when initial pressure is 200 mm at 900° K.

$12\frac{1}{2}$ %, 25 % and 50 % completion of reaction. Their figures are plotted in fig. 2, and it is seen that the rate constant calculated from the " initial " rate is lower than is consistent with the other figures. This would be expected if the reaction is accompanied by an induction period. It is intended to examine this aspect of the reaction experimentally in due course.

The observation of induction periods may be put to important uses. Apart from supplying proof that chain reactions are truly homogeneous,[6] they can provide a means of estimating the speeds of reactions not easily susceptible to direct measurement. For example, it has been shown that certain chloroethane pyrolyses [6] probably proceed by a chain mechanism of type:

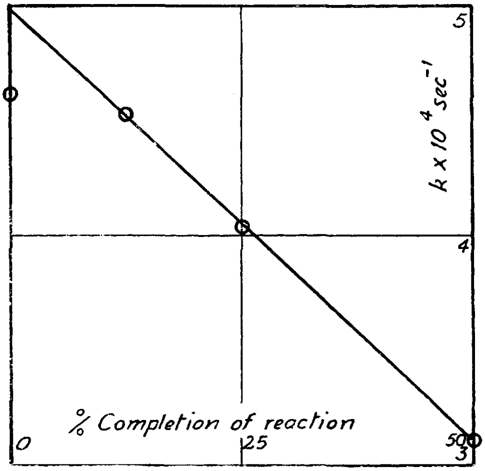

FIG. 2.—Graph of Steacie and Shane's values for rate constant of ethane decomposition as a function of the % completion of reaction at 880° K.

$$A \xrightarrow{k_6} R_1 + Cl \quad (6)$$

$$Cl + A \xrightarrow{k_7} HCl + R_2 \quad (7)$$

$$R_2 \xrightarrow{k_8} M + Cl \quad (8)$$

$$Cl + R_1 \xrightarrow{k_9} \text{products}, \quad (9)$$

from which $k = (k_6k_7k_8/k_9)^{\frac{1}{2}}$ time^{-1}. Also, from the approximate treatment of the induction periods given previously,[6]

$$I = (k_7/k_6k_8k_9)^{\frac{1}{2}}.$$

Thus $kI = k_7/k_9$ and $k/I = k_6k_8$. k and I are observable quantities and the right-hand side of each of these two latter expressions contains one rate constant of an experimentally observable process, so that the rates of steps 8 and 9 become measurable. If these equations are applied to the radical chain parts of the decompositions of 1 : 2-di-, 1 : 1 : 1-tri- and 1 : 1 : 2 :2-tetra-chloroethane,[6] the following results are obtained:

substance	k, sec^{-1}	I, sec
$CH_2Cl \cdot CH_2Cl$	$10^{10\cdot8}$ exp $(-47000/RT)$	$10^{-12\cdot4}$ exp $(44000/RT)$
$CCl_3 \cdot CH_3$	$10^{12\cdot5}$ exp $(-47000/RT)$	$10^{-14\cdot4}$ exp $(50000/RT)$
$CHCl_2 \cdot CHCl_2$	$10^{9\cdot6}$ exp $(-36500/RT)$	$10^{-13\cdot2}$ exp $(44000/RT)$

substance	k_7/k_9	k_6k_8
$CH_2Cl \cdot CH_2Cl$	$10^{-1\cdot6}$ exp $(-3000/RT)$	$10^{23\cdot2}$ exp $(-91000/RT)$
$CCl_3 \cdot CH_3$	$10^{-1\cdot9}$ exp $(3000/RT)$	$10^{26\cdot9}$ exp $(-97000/RT)$
$CHCl_2 \cdot CHCl_2$	$10^{-3\cdot6}$ exp $(7500/RT)$	$10^{22\cdot8}$ exp $(-80500/RT)$.

The trend of k_7/k_9 indicates that, with increasing chlorination, the steric factor for step 7 falls faster than that for step 9, and it appears that the radical recombination process 9 requires an appreciable energy of activation in the higher chlorinated derivatives. Also, from the values of k_6k_8, if the initial steps of the three reaction schemes have normal frequency factors, two of the three cases considered show somewhat low non-exponential terms for the unimolecular radical decomposition step 8. This conclusion is in agreement with the calculations of Trotman-Dickenson[18] for the unimolecular decompositions of the CH_2OH and CH_3OCH_2 radicals.

[1] Burnett, *Trans. Faraday Soc.*, 1950, **46,** 772.

[2] Davoud and Hinshelwood, *Nature*, 1939, **144,** 909.

[3] Allen, *J. Amer. Chem. Soc.*, 1936, **58,** 1052.

[4] Pease and Morton, *J. Amer. Chem. Soc.*, 1933, **55,** 3190.

[5] Kuchler, *Trans. Faraday Soc.*, 1939, **35,** 874.

[6] Barton and Howlett, *J. Chem. Soc.*, 1949, 155. Barton and Onyon, *J. Amer. Chem. Soc.*, 1950, **72,** 988. Barton and Howlett, *J. Chem. Soc.*, 1951, 2038. Howlett, *Trans. Faraday Soc.*, preceding paper; Barton and Head, unpublished.

[7] Dinzes, Stepukhovitch, Kyvatowskii and Frost, *J. Gen. Chem.* (*U.S.S.R.*), 1937, **7,** 1754.

[8] Staveley, *Proc. Roy. Soc. A*, 1937, **162,** 557.

[9] Hobbs and Hinshelwood, *Proc. Roy. Soc. A*, 1938, **167,** 439.

[10] Partington, *Faraday Soc. Discussions*, 1947, **2,** 114.

[11] Steacie, *Atomic and Free Radical Reactions* (Reinhold, New York, 1946).

[12] Laidler, *Chemical Kinetics* (McGraw-Hill, New York, 1950).

[13] Rice and Herzfeld, *J. Amer. Chem. Soc.*, 1934, **56,** 284.

[14] Sachsse, *Z. physik. Chem. B*, 1935, **31,** 87.

[15] Steacie and Shane, *Can. J. Res. B*, 1940, **18,** 203.

[16] The non-exponential terms of the individual rate constants were assigned after considering the following. k_1: Miller and Steacie, *J. Chem. Physics*, 1951, **19,** 73, and Gomer and Kistiakowsky, *J. Chem. Physics*, 1951, **19,** 85, have observed the rate of methyl recombination. Glasstone, Laidler and Eyring, *The Theory of Rate Processes* (N.Y. 1941), p. 260, have calculated this and the equilibrium constant between ethane and methyl radicals. k_2: Steacie, Darwent and Trost, *Faraday Soc. Discussions*, 1947, **2,** 80; Trotman-Dickenson, Birchard and Steacie, *J. Chem. Physics*, 1951, **19,** 163. k_4: Steacie, Darwent and Trost, *loc. cit.* k_5: Likely to be similar to k_4. The following aided the choice of the individual activation energies. k_1: at room temperature $D(CH_3—CH_3) \sim 85$-86. Compare Steacie, *Atomic and Free Radical Reactions* (N.Y. 1946), p. 79. To this must be added two small terms, viz. any activation energy due to methyl recombination (see ref. for A_{k_1}), and about 1 kcal/mole arising from a greater increase in heat content of two methyl groups relative to that of ethane in rising to 900° K. k_2: see ref. for A_{k_2}. k_3: Bywater and Steacie, *J. Chem. Physics*, 1951, **19,** 328 (compare also thermochemical evidence collected by Steacie, *loc. cit.*) plus small corrections as with k_1. k_4: altered from value given by Steacie, Darwent and Trost, *loc. cit.* to be consistent with assignment for k_2.

[17] It may be useful to note that the calculated induction periods would increase with increase in the value assumed for k_5, and with decrease in k_1. Changes in k_2, k_3 and k_4 have considerably less effect upon the result. It must be remembered, however, that not less than two elementary rate constants may be altered simultaneously if the theoretical and experimental overall rates are to remain in agreement.

[18] Trotman-Dickenson, *J. Chem. Physics*, 1951, **19,** 261.