# 84. *The Mechanism of Cracking. Part I. Kinetics of Inverse Diene Synthesis in Solution and in the Pure Liquid State.*

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The kinetics of the decomposition of *cyclo*pentadienebenzoquinone and of *cyclo*pentadiene-α-naphthaquinone have been measured in benzene solution, and the cracking of di*cyclo*pentadiene has been studied in paraffin solution and in the pure liquid state. The experiments were carried out at atmospheric pressure between 49° and 175°. The non-exponential factors of the velocity coefficients are of the order of magnitude of interatomic vibration frequencies, and hence it can be concluded that the inverse diene syntheses are unimolecular reactions.

THE experiments now to be described deal with the kinetics of those cracking processes which are inverse diene syntheses. The following reactions have been investigated :

*cyclo*Pentadienebenzoquinone ⟶ *cyclo*Pentadiene + Benzoquinone . . (1)
*cyclo*Pentadiene-α-naphthaquinone ⟶ *cyclo*Pentadiene + α-Naphthaquinone (2)
Di*cyclo*pentadiene * ⟶ 2 *cyclo*Pentadiene . . . . (3)

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* Cf. footnote on p. 367.

The rate of Nos. (1) and (2) has been measured colorimetrically in benzene solution. The products remained in solution and, therefore, for a calculation of the velocity coefficients, the reverse associations had to be taken into account. The velocity of reaction (3) has been studied in paraffin solution and in the pure liquid state by two different methods. The first is characterised by the fact that the *cyclo*pentadiene is so quickly removed from the reaction vessel that the back reaction could be neglected. In carrying out the experiments based on the second method the greater part of the *cyclo*pentadiene is also removed from the liquid phase, but the gaseous *cyclo*pentadiene remains in the hot reaction vessel and so the back reaction had to be considered. The velocity coefficients obtained by the two different methods agreed within the limits of the experimental error.

In solution, all the inverse diene syntheses are of the first order. In the decomposition of di*cyclo*pentadiene, no induction period occurs, and peroxidic intermediate compounds, glass powder, mercury, lead dioxide, molybdenum sulphide, and tin sulphide do not influence the rate. These observations indicate that the decomposition is not a chain reaction.

The first-order velocity coefficients obey the Arrhenius equation (cf. p. **362**). The non-exponential factors, $A$ (in sec.$^{-1}$), and the activation energies, $E$ (in kg.-cals.), are given in Table I. The $A$ factors are of the order of magnitude of interatomic vibrations, and therefore it can be concluded (Polanyi and Wigner, *Z. physikal. Chem.*, 1928, **139**, 439) that the mechanism is unimolecular.

TABLE I.

| Reaction. | Solvent. | $\log_{10} A$. | $E$. |
|---|---|---|---|
| (1) | Benzene | $12{\cdot}6 \pm 1$ | $29 \pm 1{\cdot}5$ |
| (2) | Benzene | $11{\cdot}0 \pm 1$ | $26 \pm 1{\cdot}5$ |
| (3) | Paraffin | $13{\cdot}0 \pm 0{\cdot}2$ | $34{\cdot}2 \pm 0{\cdot}4$ |

The rate of decomposition of pure liquid di*cyclo*pentadiene is given by

$$dx/dt = k(a - x)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $a$ is the concentration of the pure liquid and $n$ indicates the molecularity; $a$ does not change appreciably and is always very much greater than $x$. It follows that constant velocity coefficients must be obtained for all values of $n$, and the molecularity cannot be deduced in the usual way. For a determination of the value of $n$, ter-, bi-, and uni-molecular velocity coefficients, $k_3$, $k_2$, and $k_1$, have been calculated, by substituting in (4) the experimental values of $x$ and assuming that $n$ is 3, 2, and 1 respectively. The velocity coefficients can be represented by

$$k_n = A_n e^{E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the numerical values for six temperatures (100—155°) are given in Table VI. If the figures in the last three lines are plotted against $1/T$, parallel straight lines are obtained from which one and the same activation energy, $E = 35{\cdot}3 \pm 0{\cdot}6$ kg.-cals., can be deduced. By substituting this value in (5) the following non-exponential factors are obtained: $A_3 = 8 \times 10^{11}$ (g.-mol./l.)$^{-2}$ sec.$^{-1}$ and $A_2 = 6 \times 10^{12}$ (g.-mol./l.)$^{-1}$ sec.$^{-1}$. It has been found that the non-exponential factor of the velocity coefficient of ter- and bi-molecular reactions is much smaller than $10^{11}$ when the reactants are polyatomic molecules.* The above values of $A_3$ and $A_2$, however, are not smaller than $10^{11}$, and therefore the decomposition of pure liquid di*cyclo*pentadiene is not a ter- or a bi-molecular process. If the experimental activation energy is substituted in (5) with $n = 1$, it is found that $A_1 = 4 \times 10^{13}$ sec.$^{-1}$. This is of the same order of magnitude as the value in the last line of Table I, and so it can be concluded that the decomposition is a unimolecular reaction, not only in paraffin solution, but also in the pure liquid state.

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* The experimental evidence for this has only been published for bimolecular reactions (cf. references in *Trans. Faraday Soc.*, 1938, **34**, 128). The non-exponential factor of the velocity coefficient of (ter-molecular) reactions involving three polyatomic reactants will be discussed in a following paper. A preliminary discussion is given by Kkambata, Thesis, London, 1938, p. 59.

## EXPERIMENTAL.

*Materials.*—*cyclo*Pentadiene-benzoquinone (I) and -α-naphthaquinone (II) were prepared according to Albrecht (cf. references in Part I; J., 1935, 828), and purified by crystallisation from hexane; (I) had the correct m. p., 77°, but contained a small quantity of benzoquinone which could be estimated by colorimetric measurements; (II) melted at 114°. Di*cyclo*pentadiene was a sample from Messrs. Light (London) and was redistilled shortly before each experiment in a stream of nitrogen; b. p. 70·0°/22 mm., m. p. 30—31°. The paraffin was the same sample as that used for the experiments described in the preceding paper. Benzene and the substances mentioned in Table VII were the purest commercial samples. The glass powder was made from the same material as that used for the reaction vessel.

*Colorimetric Measurements.*—These were carried out with the Zeiss Stuphenphotometer and filter $S_{47}$. The molar extinction coefficient of (I) in benzene is 0·0578 l./g.-mol.-cm. (cf. J., 1935, *loc. cit.*); (II) is colourless, and the molar extinction coefficients of benzoquinone and α-naphthaquinone in benzene are 17·0 and 9·96 l./g.-mol.-cm. respectively. These figures show that the decomposition of (I) and (II) is accompanied by a change of colour, and so the velocity coefficients of the inverse diene syntheses (1) and (2) can be determined by carrying out colorimetric measurements at known time intervals. The colour was measured in a cell of the form already described (Fig. 2; *Nature*, 1934, **134**, 101); its thickness was 10·9 cm., and its temperature could be kept constant to within ± 0·1°. Below 80°, water thermostats, and above this temperature oil thermostats, were used. The colour measurements mentioned on p. 378 were carried out by using a cell 1·00 cm. thick.

*Reaction* (1).—The velocity coefficients were calculated from

$$k = [dx/dt + k'(b + x)x]/(a - x) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

where $a$ and $b$ are the initial molar concentrations of (I) and benzoquinone respectively, $b + x$ is the concentration of benzoquinone at time $t$, and $k'$ is the velocity coefficient of the reverse reaction (cf. Part IV; J., 1936, 1028). Details of a typical experiment are:

Temp., 74·0°; $a = 0{\cdot}115$; $b = 0{\cdot}000299$; $k' = 8{\cdot}7$ l. g.-mol.$^{-1}$ min.

| | | | | | | |
|---|---|---|---|---|---|---|
| Time, min. | 20 | 40 | 80 | 120 | 200 | 360 |
| Extinction coefficient, cm.$^{-1}$ | 0·030 | 0·036 | 0·044 | 0·051 | 0·060 | 0·078 |
| $k \times 10^4$, min.$^{-1}$ | 1·4 | 1·3 | 1·4 | 2·0 | 2·1 | 4·8 |

The increase of the velocity coefficient is due to a consecutive reaction between (I) and *cyclo*pentadiene leading to di*cyclo*pentadienebenzoquinone (Part IV, *loc. cit.*). Hence the correct velocity coefficients are obtained by extrapolating the observed values to zero time. The statement that reaction (1) is of the first order is based on the fact that the extrapolated velocity coefficients, $k_0$, do not depend on the initial concentrations. This is shown by the following figures obtained from experiments at 74·0°.

| | | | |
|---|---|---|---|
| $a$ (g.-mol./l.) | 0·206 | 0·115 | 0·0187 |
| $k_0 \times 10^4$ (min.$^{-1}$) | 1·4 | 1·2 | 1·3 |

The mean values of the extrapolated velocity coefficients as obtained at the various temperatures are given in Table II.

### TABLE II.

*Decomposition of* cyclo*Pentadienebenzoquinone in Benzene.*

| | | | | | | |
|---|---|---|---|---|---|---|
| Temp. | 78·6° | 74·0° | 69·5° | 63·9° | 59·4° | 54·6° |
| $k_0 \times 10^4$ (min.$^{-1}$) | 3·3 | 1·3 | 0·82 | 0·48 | 0·24 | 0·13 |

*Reaction* (2).—The velocity coefficients were calculated from

$$k = \frac{2{\cdot}30}{t\sqrt{1 + 4Ka}} \log_{10} \frac{x(1 - \sqrt{1 + 4Ka}) - 2a}{x(1 + \sqrt{1 + 4Ka}) - 2a} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

$a$ is the initial concentration of (II) and $x$ is the concentration of α-naphthaquinone at time $t$; $K$, the equilibrium constant of reaction (2), is defined by

$$K = (a - X_e)/X_e^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

where $a - X_e$ is the equilibrium concentration of (II). The results of the equilibrium measurements are given below, concentrations being in g.-mol./l., and ε being the extinction coefficient (in cm.$^{-1}$) at infinite time.

| Temp. | *a*. | ε. | $X_e \times 10^3$. | $\log_{10} K$. |
|---|---|---|---|---|
| 78·9° | 0·318 | 0·0680 | 6·82 | 3·83 |
| 78·7 | 0·149 | 0·0460 | 4·62 | 3·83 |
| 79·0 | 0·116 | 0·0398 | 4·00 | 3·85 |
| 78·5 | 0·0536 | 0·0280 | 2·81 | 3·81 |

| Temp. | *a*. | ε. | $X_e \times 10^3$. | $\log_{10} K$. |
|---|---|---|---|---|
| 69·0° | 0·189 | 0·0369 | 3·71 | 4·10 |
| 59·0 | 0·203 | 0·0278 | 2·79 | 4·41 |
| 48·6 | 0·246 | 0·0203 | 2·00 | 4·79 |

The results of the rate measurements are given in Table III. In section (A) are the data for a typical experiment at 78·5°; *a* was 0·0536 g.-mol./l. In section (B) are velocity coefficients deduced from experiments at 78·5° and with various initial concentrations. In section (C) are the velocity coefficients at lower temperatures. In all these sections, *k* is in terms of min.$^{-1}$.

TABLE III.

*Decomposition of* cyclo*Pentadiene-α-naphthaquinone in Benzene.*

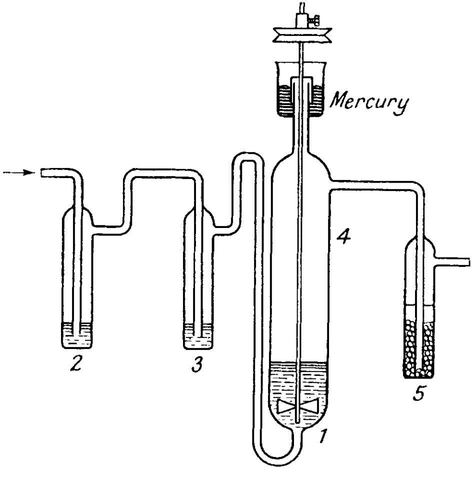
| | | | | | |
|---|---|---|---|---|---|
| A | Time (min.) | 40 | 60 | 120 | 180 |
| | ε (cm.$^{-1}$) | 0·00840 | 0·0120 | 0·0200 | 0·0244 |
| | $k \times 10^4$ | 4·1 | 4·0 | 3·9 | 3·7 |

| | | | | | |
|---|---|---|---|---|---|
| B | *a* | 0·318 | 0·149 | 0·116 | 0·0536 |
| | $k \times 10^4$ | 4·1 | 4·2 | 4·2 | 4·0 |
| C | Temp. | 69·0° | 59·0° | 48·6° | |
| | $k \times 10^4$ | 1·7 | 0·48 | 0·12 | |

At the end of all the measurements involving (I) and (II) the solvent was evaporated, and the residue recrystallised from hexane; 13 g. of (I) were obtained from 14 g. of the residue of reaction (1), and 9 g. of (II) from 11 g. of that of reaction (2). These figures show that under the conditions of the kinetic measurements no isomerisation of the reactants occurs.

*Reaction* (3).—*First method.* The measurements were carried out in the apparatus shown in Fig. 1. The reaction vessel (1), of about 200 cm.$^3$ capacity, contained either a solution of di*cyclo*pentadiene (III) in paraffin or pure liquid (III), and was introduced into the thermostat up to the mark 4. The wash flasks (2) and (3) contained liquid (III), and wash flask (5), which was kept at about 10°, contained glass beads and a known amount of benzoquinone in benzene. The *cyclo*pentadiene formed during the decomposition of (III) had to be removed from the reaction vessel as quickly as possible, and therefore a stream of nitrogen was passed through the apparatus in the direction of the arrow, and the contents of (1) were stirred at a speed of 100—140 r.p.m. The *cyclo*pentadiene was absorbed in the wash flask (5), where it reacted with the benzoquinone to form nearly colourless *cyclo*pentadienebenzoquinone. If the colour of the benzoquinone solution after the reaction with the *cyclo*pentadiene is determined, the amount of (III) which is decomposed and, therefore, also the velocity coefficient of reaction (3), can be deduced. Control experiments showed that: (*a*) the amount of (III) which decomposed before the beginning of the measurement, during the attainment of the temperature equilibrium, is negligibly small; (*b*) the amount of *cyclo*pentadiene which remained dissolved in the reaction mixture at the end of the measurement is also negligibly small; (*c*) one wash flask containing the benzoquinone solution was sufficient to absorb all the *cyclo*pentadiene; (*d*) the colour of the benzoquinone solution remained unchanged if the reaction vessel contained pure paraffin at 155° and a stream of nitrogen was passed through the apparatus, which was stirred as mentioned above.

FIG. 1.



*Measurements in paraffin solution.* Two typical experiments and the mean values of the velocity coefficients at the various temperatures are in Table IV (concentrations in g.-mol./l.). The velocity coefficients were calculated from

$$k = (2\ 30/t)\log_{10}a/(a - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where *a* and *a* − *x* are the concentrations of (III) at zero time and time *t* respectively. In all the experiments, 25·0 cm.$^3$ of the paraffin solution were used.

TABLE IV.

| Temp. | *t*, min. | Initial concn. of $C_{10}H_{12}$. | $C_6H_4O_2$ sol. in flask (5), cm.$^3$. | Concn. of $C_6H_4O_2$. Before reaction with $C_5H_6$. | Concn. of $C_6H_4O_2$. After reaction with $C_5H_6$. | *x*. | *k* (min.$^{-1}$). |
|---|---|---|---|---|---|---|---|
| 155° | 47 | 0·517 | 15·0 | 0·467 | 0·300 | 0·052 | $2·2 \times 10^{-3}$ |
| | 92 | 0·513 | 25·0 | 0·396 | 0·218 | 0·089 | $2·2 \times 10^{-3}$ |
| | 93 | 0·518 | 15·0 | 0·467 | 0·173 | 0·097 | $2·1 \times 10^{-3}$ |
| | 191 | 0·538 | 30·0 | 0·474 | 0·219 | 0·154 | $1·8 \times 10^{-3}$ |
| | 99 | 1·000 | 35·0 | 0·467 | 0·200 | 0·190 | $2·1 \times 10^{-3}$ |
| 120 | 113 | 1·328 | 10·0 | 0·100 | 0·0644 | 0·0071 | $4·6 \times 10^{-5}$ |
| | 234 | 1·229 | 10·0 | 0·100 | 0·0311 | 0·0138 | $4·9 \times 10^{-5}$ |
| | 335 | 1·229 | 10·0 | 0·100 | 0·0013 | 0·0197 | $4·9 \times 10^{-5}$ |

| Temp. .................... | 120° | 135° | 145° | 155° | 165° | 175° |
|---|---|---|---|---|---|---|
| Initial concn. of $C_{10}H_{12}$ | 1·23, 1·33 | 1·328—1·97 | 1·04 | 0·251—1·000 | 0·502 | 0·502 |
| *k* (min.$^{-1}$) ............... | $4·8 \times 10^{-5}$ | $2·6 \times 10^{-4}$ | $7·2 \times 10^{-4}$ | $2·1 \times 10^{-3}$ | $4·0 \times 10^{-3}$ | $8·0 \times 10^{-3}$ |

*Measurements in the pure liquid state.* Data for a typical experiment at 125° are given in Table V. The concentration of pure liquid (III) was calculated from the densities (see this vol., p. 369). In all the experiments flask (5) contained 10·0 cm.$^3$ of the benzoquinone solution.

TABLE V.

| $C_{10}H_{12}$ in reaction vessel, cm.$^3$. | *t*, min. | Concn. of $C_6H_4O_2$. Before reaction with $C_5H_6$. | Concn. of $C_6H_4O_2$. After reaction with $C_5H_6$. | $k_1 \times 10^4$ (min.$^{-1}$) [in equation (4), $n = 1$]. |
|---|---|---|---|---|
| 17·7 | 60 | 0·500 | 0·377 | 0·9 |
| 32·3 | 120 | 0·500 | 0·0536 | 0·9 |
| 17·6 | 185 | 0·775 | 0·290 | 1·1 |
| 17·4 | 253 | 0·775 | 0·153 | 1·0 |

A number of experiments were carried out in which the stirring speed varied from 135 to 1500 r.p.m. No effect could be observed, and hence it can be concluded that the rate-determining step is the decomposition of (III) and not the transition of *cyclo*pentadiene from the liquid to the gaseous phase.

A sample of (III), purified as described above, was kept at room temperature for 3 weeks in a desiccator, the tap of which was open. When 0·01 g. of this sample was shaken with an excess of an aqueous solution of ferrous sulphate and ammonium thiocyanate a deep red colour was immediately produced. Hence it can be concluded (cf. Kharasch, *J. Amer. Chem. Soc.*, **1933**, **55**, 2468) that during exposure to air a certain amount of di*cyclo*pentadiene peroxide is formed (cf. also Engler and Frankenstein, *Ber.*, **1901**, **34**, 2938); 9·7 g. of the di*cyclo*pentadiene which had been exposed to air and 14·5 g. of pure di*cyclo*pentadiene were introduced into the reaction vessel of Fig. 1, and the velocity of the decomposition of the mixture was determined at 125°. The velocity coefficient agreed with the values given in Table V, so peroxidic intermediate compounds do not influence the kinetics.

The concentration of pure liquid (III) and the mean values of the velocity coefficients at the various temperatures are in Table VI. All the velocity coefficients were calculated in the appropriate units involving g.-mol./l. and min. for the values $n$ = 3, 2, and 1 in equation (4).

TABLE VI.

*Decomposition of Pure Liquid Di*cyclo*pentadiene at Various Temperatures.*

| Temp. .................................... | 100° | 110° | 125° | 130° | 140° | 155° |
|---|---|---|---|---|---|---|
| Concn. of pure liquid $C_{10}H_{12}$ (g.-mol./l.) ............................ | 6·79 | 6·70 | 6·58 | 6·53 | 6·44 | 6·30 |
| $-\log_{10}k_3$ .................................. | 7·060 | 6·658 | 5·638 | 5·456 | 5·046 | 4·398 |
| $-\log_{10}k_2$ ............................. | 6·229 | 5·824 | 4·824 | 4·638 | 4·215 | 3·602 |
| $-\log_{10}k_1$ ............................. | 5·398 | 5·000 | 4·000 | 3·824 | 3·409 | 2·796 |

*Reaction* (3).—*Second method.* The measurements were carried out in the apparatus shown in Fig. 2. The reaction vessel (100—300 cm.$^3$) contained in each experiment 25·0 cm.$^3$ of a solution of (III) in paraffin. It was immersed in the thermostat up to the mark 2, stirred, and tap (3) was connected with a suction pump in order to remove the *cyclo*pentadiene formed during the attainment of the temperature equilibrium. At zero time the tap was closed, mercury was introduced into (4), and the gaseous *cyclo*pentadiene, which is formed during the decomposition of (III), was measured in the burette (5) which was kept at 52° by pumping water from (*a*) to (*b*). The data for a typical experiment are given below. The initial concentration of (III) was 0·73 g.-mol./l., the temperature 155°, the volume of the reaction vessel 200 cm.$^3$, the stirring speed 750 r.p.m., and the pressure 738 mm.

FIG. 2.

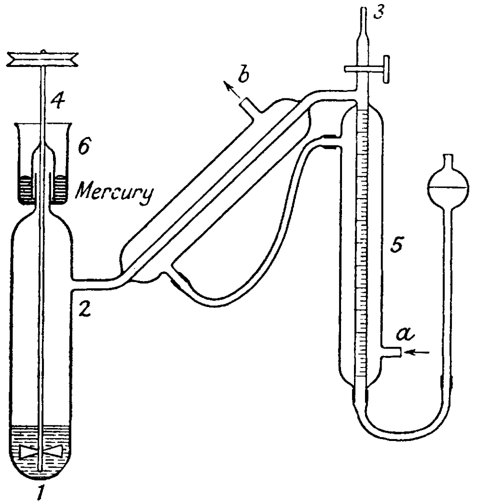
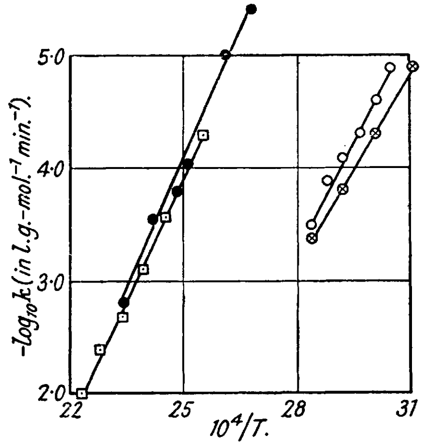


FIG. 3.



○ = cyclo*Pentadienebenzoquinone.*
⊗ = cyclo*Pentadiene-α-naphthaquinone.*
□ = *Di*cyclo*pentadiene in paraffin.*
● = *Pure liquid di*cyclo*pentadiene.*

| Time, min. | 5 | 10 | 15 | 20 | 25 | 30 | 40 | 60 | 80 | 170 |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_5H_6$, cm.$^3$ | 4·3 | 7·6 | 10·8 | 13·2 | 15·2 | 17·0 | 19·8 | 23·4 | 25·4 | 27·0 |
| $x' \times 10^2$ (g.-mol./l.) | 0·61 | 1·08 | 1·54 | 1·88 | 2·16 | 2·42 | 2·78 | 3·33 | 3·61 | 3·89 |
| $k' \times 10^3$ (min.$^{-1}$) | 1·7 | 1·3 | 1·2 | 0·93 | 0·77 | 0·71 | 0·49 | 0·38 | 0·19 | 0·04 |

For the calculation of the velocity coefficients, $k'$, it was assumed that (1) the reverse reaction (association of *cyclo*pentadiene) can be neglected, and (2) the whole of the *cyclo*pentadiene formed during the decomposition of (III) evaporates. Consequently, the velocity coefficients were calculated from

$$k' = (\mathrm{d}x'/\mathrm{d}t)/(a - x') \quad . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

where $a$ and $a - x'$ are the concentrations of (III) at zero time and time $t$ respectively, and $x'$ can be deduced from the data in the second line. It will be seen that the $k'$ values decrease rapidly, because, under the conditions of these measurements, the reverse reaction cannot be neglected. In order to eliminate the influence of the reverse reaction the observed $k'$ values were extrapolated to zero time. The velocity coefficients obtained in this way are designated by $k_0'$ and are given below.

| Temp. | 145° | 155° | 165° | 175° |
|---|---|---|---|---|
| $a$ (g.-mol./l.) | 1·0 | 0·73 | 0·50 | 0·14 |
| $k_0'$ (min.$^{-1}$) | $6{\cdot}7 \times 10^{-4}$ | $2{\cdot}2 \times 10^{-3}$ | $5{\cdot}0 \times 10^{-3}$ | $8{\cdot}0 \times 10^{-3}$ |

The values in the last line and the velocity coefficients of Table IV agree within the limits of the combined experimental error, and hence it can be concluded that under the conditions of these measurements the fraction of the *cyclo*pentadiene which does not evaporate is negligibly small. The velocity coefficients of the preceding table relate to the earliest stage of the decomposition of di*cyclo*pentadiene, whereas those in Table IV relate to a later stage. Their agreement proves that no induction period occurs.

The influence of added substances was investigated at 155°, a 0·70 M-solution of (III) in paraffin being used. The volume of the reaction vessel was 300 cm.$^3$, the stirring speed 750—1000 r.p.m., and the pressure 735—765 mm. The volumes of *cyclo*pentadiene given in Table VII were measured in burette 5,30 minutes after tap 3 had been closed.

TABLE VII.

| Added substance: | None. | Glass powder. | Mercury. | $PbO_2$. | $CaCO_3$. | $MoS_2$. | $SnS_2$. |
|---|---|---|---|---|---|---|---|
| Weight, g. .................. | — | 1 | 4 | 3 | 0·6 | 1·3 | 0·8 |
| $C_5H_6$, cm.$^3$ .................. | 19 | 19 | 19 | 21 | 19 | 19 | 19 |

In Fig. 3 the decadic logarithm of the velocity coefficients of Tables II, III, IV, and VI (last line) were plotted against the reciprocal absolute temperature The four graphs were used to calculate the activation energies in Table I and on p. 376.

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