**83.** *The Mechanism of Additions to Double Bonds. Part VIII. The Equilibrium of Gaseous Associations.*

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The non-exponential factor of the equilibrium constant of the reaction 2 *cyclo*pentadiene (gas) $\rightleftharpoons$ di*cyclo*pentadiene (gas) has been experimentally determined, and the translational and rotational partition functions have been calculated both for the reactant and for the product. It has been deduced that, at 80°, the vibrational partition function of di*cyclo*pentadiene is at least 500 times larger than the square of that of *cyclo*pentadiene.

IN this communication the following gaseous equilibrium is discussed :

*cyclo*Pentadiene.   *cyclo*Pentadiene.   Di*cyclo*pentadiene.* . . (1)
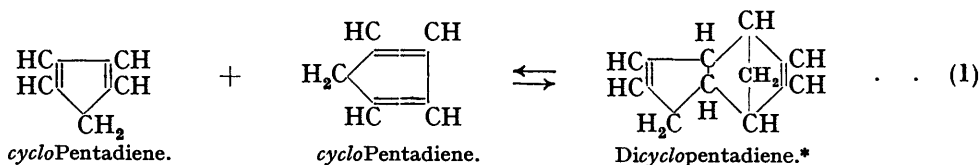
The molecules are treated as perfect gases, and the equilibrium constant is defined by

$$K = \text{Vol. concn. of di}cyclo\text{pentadiene}/(\text{Vol. concn. of }cyclo\text{pentadiene})^2 = De^{-\Delta E\,RT} \quad (2)$$

ΔE is the energy change and, if the volume concentrations are expressed in g.-mol./l., the non-exponential factor can be represented (cf. Fowler, " Statistical Mechanics," Cambridge, 1936) by

$$D = N\text{Tr}_c\text{Ro}_c\text{Vi}_c/1000\text{Tr}_a{}^2\text{Ro}_a{}^2\text{Vi}_a{}^2 \quad . \quad . \quad . \quad . \quad (3)$$

where N is Avogadro's number, and Tr, Ro, and Vi are translational, rotational, and vibrational partition functions, each referred to an energy zero being that of the lowest state for the relevant degree of freedom. The subscripts a and c refer in (3) and in all the following equations to *cyclo*pentadiene and di*cyclo*pentadiene respectively. The experiments and calculations now to be described enable a comparison to be made between the vibrational partition functions of di*cyclo*pentadiene and the square of that of *cyclo*pentadiene.

Results and Discussion.—The non-exponential factor, D [see (2)], has been deduced from the kinetics of the formation and decomposition of di*cyclo*pentadiene in paraffin and from the solubilities of gaseous *cyclo*pentadiene and di*cyclo*pentadiene in paraffin. The kinetic measurements were carried out between $-1°$ and $175°$, and the solubilities between $27°$ and $111°$ (cf. preceding paper). In this temperature range $\log_{10} D$ is equal to -7.1 ± 0.7 if the concentrations are expressed in g.-mol./l.

The translational partition functions (the volume factor being omitted) are given by

$$\text{Tr} = \text{tr}T^{3/2} = (2\pi\Sigma mkT)^{3\,\text{P}}/h^3 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Here, and in all the following equations, T, k and h are respectively the absolute temperature and Boltzmann's and Planck's constants and Σm is the mass of the molecule. At $80°$ the translational partition functions of *cyclo*pentadiene and di*cyclo*pentadiene are 6.4×10^{26} cm.$^{-3}$ and 18×10^{26} cm.$^{-3}$, respectively.

The rotational partition functions can be represented by †

$$\text{Ro} = \text{ro}T^{3/2} = 8\pi^2(8\pi^3 I'I''I''')^{1/2}(kT)^{3/2}/h^3 s \quad . \quad . \quad . \quad (5)$$

Here, s is a symmetry number, which is 2 for *cyclo*pentadiene and 1 for di*cyclo*pentadiene, and I', I'', and I''' are the principal moments of inertia, which can be calculated if the centre of gravity of the molecules and the co-ordinates x, y, and z of all the atoms, of the mass m, are known. The principal moments of inertia can be deduced from the following secular equation,‡ if x, y, and z refer to an arbitrary system of rectangular co-ordinates the origin of which coincides with the centre of gravity.
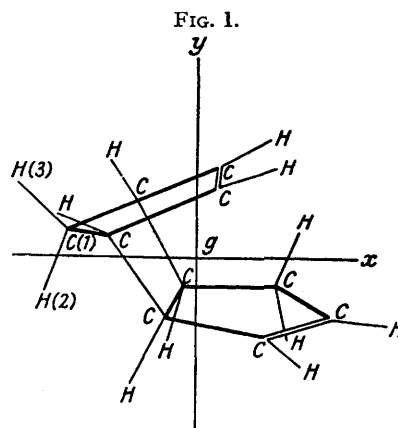
$$\begin{vmatrix} \Sigma m(y^2+z^2) - I & \Sigma mxy & \Sigma mxz \\ \Sigma mxy & \Sigma m(z^2+x^2) - I & \Sigma myz \\ \Sigma mxz & \Sigma myz & \Sigma m(x^2+y^2) - I \end{vmatrix} = 0 \quad . \quad . \quad (6)$$

* Compare footnote on p. 367.

† The nuclear spin factors have been omitted because they cancel in (3).

‡ Cf., *e.g.*, Planck, " Allgemeine Mechanik," 1928, § 142; Frank und von Mises, " Die Differential und Integralgleichungen der Mechanik und Physik," 1930, Chapter II, § 4; Bürklen, " Mathematische Formelsammlung," 1936, p. 16. The method for the determination of the position of the centre of gravity is described in " Handbuch der Experimental Physik," 1926, Vol. II, p. 186.

(6) is a cubic equation, the roots of which are the principal moments of inertia. Models of steel wire, constructed to scale, were used for the determination of the x, y, and z values of all the atoms in *cyclo*pentadiene and di*cyclo*pentadiene. In these models the lengths of the C–C, C=C, and C–H bonds were 15, 13, and 11 cm., and hence the dimensions were so large that the various co-ordinates could be directly measured by using a ruler.* The model of *cyclo*pentadiene is represented in Part I (J., 1935, 833), and that of di*cyclo*pentadiene in Fig. 1, in which the position of the centre of gravity (g) and the direction of the x and y axes are also shown. The principal moments of inertia and the rotational partition functions, at 80°, are given in Table I. The value in parentheses was calculated on the assumption that the atoms 1, 2, and 3 of di*cyclo*pentadiene had other positions than those shown in the figure.

The vibrational partition functions can be represented by a product of n factors

$$\mathrm{Vi} = \Pi_n 1/(1 - e^{-h\nu_n/kT}) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where n is the number of normal modes of vibration (27 for *cyclo*pentadiene and 60 for di*cyclo*pentadiene) and the ν's are the corresponding frequencies. The vibrational partition functions cannot be deduced either theoretically or

Fig. 1.

Model of dicyclopentadiene. The positions of the carbon and hydrogen atoms are indicated by C and H. One carbon atom and two hydrogen atoms are numbered for further reference.

TABLE I.

	Principal moments of inertia, in g. cm.^{2} × 10^{39}.	Rotational partition functions.
*cyclo*Pentadiene	11; 17; 17	4·7 × 10^4
Di*cyclo*pentadiene..............	30 (42); 43; 51	43 × 10^4

empirically because the normal modes of vibration and the specific heats of *cyclo*pentadiene and of di*cyclo*pentadiene are unknown but the ratio

$$\frac{\text{Vibrational partition function of di}\mathit{cyclo}\text{pentadiene}}{\text{Square of vibrational partition function of }\mathit{cyclo}\text{pentadiene}} \quad . \quad . \quad . \quad (8)$$

can be calculated. For this, the equilibrium constant (2) is represented by

$$K = GT^{-3}e^{-\Delta E'/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The exponential and the non-exponential factors are given by

$$\Delta E' = \Delta E + 3RT$$
$$G = N\mathrm{tr}_c\mathrm{ro}_c\mathrm{Vi}_c/1000\mathrm{tr}_a{}^2\mathrm{ro}_a{}^2\mathrm{Vi}_a{}^2 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

N has the same meaning as in (3) and tr and ro are defined by (4) and (5). G can be deduced from the experimentally determined non-exponential factor of (2) and tr and ro are obtained from the data given on p. 372 and in Table I. It is thus found that, at 80°, the decadic logarithm of (8) is 3·4 ± 0·7. The vibrational partition function of di*cyclo*pentadiene is, therefore, at least 500 times larger than the square of that of *cyclo*pentadiene.

It can be concluded from consideration of models that *cyclo*pentadiene is a stiffer molecule than di*cyclo*pentadiene because the part of the di*cyclo*pentadiene molecule above the x axis (cf. Fig. 1) will vibrate relatively to the part below the x axis. The frequencies of such vibrations must be very low, and hence it is probable that some frequencies of di*cyclo*pentadiene are lower than the lowest frequencies of *cyclo*pentadiene. It is obvious that the vibrational partition functions must become large if all or some of the frequencies are low and, therefore, the result of the above calculation is qualitatively understandable.

* Numerical values of the co-ordinates are given by Khambata, Thesis, London, 1938, pp. 77, 79,

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<center>EXPERIMENTAL.</center>

Kinetics of Formation of Dicyclopentadiene in Paraffin.—*cyclo*Pentadiene was redistilled in the apparatus described in Part I (*loc. cit.*) shortly before each experiment, and the paraffin was " sample 2 " (cf. preceding paper, p. 369). For some experiments the paraffin was shaken successively with potassium permanganate, sulphuric acid, alkali, and water and then carefully dried, but this treatment had no influence on the two parameters of the velocity coefficients. The measurements at − 1° were carried in the thermostat described by Benford and Ingold (J., 1938, 933); the other measurements were carried out in an oil thermostat.

The rate of polymerisation of *cyclo*pentadiene in paraffin was calculated from

$$\text{velocity coefficient} = x/at(a - x) \qquad \ldots \ldots \quad (11)$$

where a is the initial concentration of *cyclo*pentadiene and $a - x$ is the concentration at time t. The experimental determination of a and $a - x$, up to 110°, was carried out by using the same technique as that described in Part IV (J., 1936, 1030), but above 110° a different method had to be used. A *cyclo*pentadiene solution of approximately known concentration was introduced into several measuring flasks. These were carefully stoppered, simultaneously introduced into the thermostat, and after about 10 minutes the solutions were made up to the mark and the flasks were again carefully stoppered. At zero time the first flask was put into ice-water and at known time intervals the other flasks were treated likewise. The contents of the flasks were transferred into larger measuring flasks, which were made up to the mark with benzene after an excess of a solution of *p*-benzoquinone in benzene had been added. After all the *cyclo*pentadiene had reacted, the excess of benzoquinone was determined at room temperature as already described (*ibid.*). In order to calculate a and $a - x$, the volume contraction of the solution between the temperature of the kinetic measurement and room temperature had to be determined. It was found that the coefficient of thermal expansion agreed with that given on p. 370 of the preceding paper. The colorimetric determination of benzoquinone was carried out in an approximately 50% mixture of paraffin and benzene, in which its molar extinction coefficient agrees with that in benzene solution. In all runs the velocity coefficients as calculated from (11) were constant. Further constant velocity coefficients at various initial concentrations were obtained.

Two typical experiments and the mean values of all the other velocity coefficients are given in Table II, concentrations being expressed in g.-mol./l. In calculating the velocity coefficients at 172°, the reverse reaction (cf. following paper) had to be taken into account, but at all the

<center>TABLE II.</center>

Rate Measurements in Paraffin : Typical Experiment, and Summary of Results.

Initial concn. of C_5H_6 (in g.-mol./l.) = 3·076 in (1), 0·0295 in (2). Temp. = 35° in (1), 136° in (2).

Conc. of $C_6H_4O_2$.

	t, mins.	C_5H_6 soln., cm.³.	Before reaction with C_5H_6.	After reaction with C_5H_6.	Concn. of C_5H_6 at time t.	100× Vel. coeff., l./g.-mol.-min.
	900	0·300	0·1266	0·0794	1·57	0·035
	1381	0·299	0·1068	0·0718	1·18	0·033
(1)	2399	0·300	0·1059	0·0810	0·817	0·035
	3840	0·300	0·1009	0·0810	0·663	0·031
	5775	0·500	0·0979	0·0762	0·434	0·034
	0	—	0·0176	0·00180	0·0295	—
	48	—	0·0147	0·00425	0·0195	37
(2)	94	—	0·0118	0·00357	0·0153	34
	138	—	0·00882	0·00296	0·0110	41
	284	—	0·00589	0·00229	0·00673	40

	Temp.:	− 1°.	35°.	55·5°.	80·2°.	110°.	136°.	172°.
Initial concn. of C_5H_6		6·587	3·076	0·0846	0·0260	0·208	0·0250, and 0·0295	0·0160
Vel. coeff.		$5·9 \times 10^{-6}$	$3·4 \times 10^{-4}$	$1·8 \times 10^{-3}$	$1·2 \times 10^{-2}$	$8·5 \times 10^{-2}$	0·40	1·8

other temperatures this could be neglected. In Expt. (1) the *cyclo*pentadiene solution was pipetted into a 10·0 cm.³ measuring flask containing the excess of benzoquinone. In Expt. (2) the volume of the reaction mixture was 50·0 cm.³ at 136° and 46·5 cm.³ at room temperature. The reaction mixture was diluted 2—15-fold before the concentration of benzoquinone was colorimetrically determined. Owing to the great dilution it was necessary to keep the reaction

mixture for about a week at room temperature before the benzoquinone concentration remained constant. During this time the solution had to be kept in the dark to prevent a photochemical decomposition of the benzoquinone.

In Fig. 2 the logarithm of the velocity coefficient is plotted against the reciprocal absolute temperature; as a straight line is obtained, it can be concluded that the Arrhenius equation, velocity coefficient $= A e^{-E/RT}$, is obeyed.

The stoicheiometric equation of the polymerisation of *cyclo*pentadiene, both in the gas phase and in the pure liquid state, is given (cf. Part VI, this vol., p. 366) by a simple dimerisation. In both states this is a bimolecular process (cf. also Part IX). The two parameters A and E of the bimolecular velocity coefficients and those deduced from the data in Table II are similar, and therefore it can be concluded that the velocity coefficients of Table II relate to the dimerisation and that the formation of di*cyclo*pentadiene in paraffin is a bimolecular process.

Fig. 2.

Kinetics of Decomposition of Dicyclopentadiene in Paraffin.—It will be shown in the following paper that the reverse reaction $C_{10}H_{12} \longrightarrow 2C_5H_6$ is a unimolecular process. The velocity coefficient (in sec.$^{-1}$) is given by $10^{13\cdot0 \pm 0\cdot2} e^{(-34200 \pm 400)/RT}$.

Equilibrium in Paraffin.—The constants of equilibrium (1) in paraffin solution can be calculated from the figures given in Table II and from the preceding expression. As the coefficient of thermal expansion of paraffin is known (cf. preceding paper, p. 370), the total heat, which is $H_{\text{Paraffin}} = -17\cdot3 \pm 0\cdot6$ kg.-cals. per g.-mol., can be deduced. If this value is substituted in equation (5) of the preceding paper it is found that $\log_{10} B_{\text{Paraffin}} = -6\cdot2 \pm 0\cdot3$, where B is in l./g.-mol.

Equilibrium in the Gas Phase.—If the above value for B_{Paraffin} and the C factor of the solubilities of gaseous *cyclo*pentadiene and di*cyclo*pentadiene are substituted in equation (11) of the preceding communication, it is found that $\log_{10} B_g = -7\cdot5 \pm 0\cdot7$, and the D value given on p. 372 can be deduced.

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