85. *The Mechanism of Additions to Double Bonds. Part IX. Kinetics of the Association of* cyclo*Pentadiene in Carbon Tetrachloride Solution and in the Pure Liquid State.*

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The association of *cyclo*pentadiene in carbon tetrachloride solution is a reaction of the second order, the mechanism of which is bimolecular, and the kinetics are not influenced by peroxides or acetonitrile. The association of pure liquid *cyclo*pentadiene is also bimolecular but the molecularity and the order do not agree at all temperatures. This is due to the fact that the " solvent " is *cyclo*pentadiene at zero time but di*cyclo*pentadiene at the end of the runs.

THE stoicheiometric equation of the thermal polymerisation of *cyclo*pentadiene in carbon tetrachloride solution or in the pure liquid state is given, under certain conditions (cf. p. **366**), by

$$2\ \textit{cyclo}\text{Pentadiene} \longrightarrow \text{Di}\textit{cyclo}\text{pentadiene}\ * \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this communication the kinetics of the association are studied, the results are compared with those deduced from previous measurements, and an attempt is made to determine the mechanism.

The velocity coefficients have been calculated from

$$k = x/at(a - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where a and $a - x$ are the concentrations of *cyclo*pentadiene at zero time and time t respectively, which can be determined by vapour-pressure and refractivity measurements (Barrett and Burrage, *J. Physical Chem.*, 1933, **37**, 1029; Stobbe and Reuss, *Annalen*, 1912, **391**, 151; Schultze, *J. Amer. Chem. Soc.*, 1934, **56**, 1552; Harkness, Kistiakowsky, and Mears, *J. Chem. Physics*, 1937, **5**, 682). The analysis can also be carried out by adding the reaction mixture to an excess of *p*-benzoquinone (Part IV; J., 1936, 1028); when the bimolecular association

$$\textit{cyclo}\text{Pentadiene} + \text{Benzoquinone} \longrightarrow \textit{cyclo}\text{Pentadienebenzoquinone} \quad . \quad . \quad (3)$$

is complete, the excess of the benzoquinone is colorimetrically determined. Further, an attempt has been made to use an analytical method based on the following reactions

$$\textit{cyclo}\text{Pentadiene} + m\,\text{Br} \longrightarrow \text{Products} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\text{Di}\textit{cyclo}\text{pentadiene} + n\,\text{Br} \longrightarrow \text{Products} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

in which the products are mixtures depending on the experimental conditions. If it be assumed that

$$m_0 = m_t = n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

then it can be deduced that the velocity coefficient is given by

$$k = (V_0 - V_t)/at(V_t - \tfrac{1}{2}V_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

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* Cf. footnote on p. 367.

where V is the volume of a bromine solution which is used, and the subscripts in (6) and (7) refer to zero time or time t. It will be shown below that the k values deduced from (2) and (7) are not equal.

Results and Previous Work.—The velocity coefficients in Tables I, III, IV, VII, IX, and X relate to the formation of di*cyclo*pentadiene and those of Table II to that of *cyclo*pentadienebenzoquinone (cf. Part I; J., 1935, 828). Concentrations are given in g.-mols./l. and k in the units l. g.-mol.$^{-1}$ min.$^{-1}$.

TABLE I.

Association of cyclo*Pentadiene in Carbon Tetrachloride at 25°. Influence of Oxygen.*

No. :	1.	2.	3.	4.	5.	6.	7.
Concn. of O_2 in reaction mixture at $t = 0$	3×10^{-3}		$<2 \times 10^{-6}$			$>10^{-6} <10^{-3}$	
a	1·236	1·637	1·24	1·64	3·69	1·051	2·725
$k \times 10^5$	9·4±1·5	6·9±1·0	7·7±0·8	9·0±1·0	8·8±0·8	8·0±0·7	7·9±0·7
Kharasch test	+	+	—	—	—		

TABLE II.

Formation of cyclo*Pentadienebenzoquinone in Benzene at 14°. Influence of Oxygen.*

No.	Concn. of O_2 in reaction mixture at $t = 0$.	Initial concns. C_5H_6.	$C_6H_4O_2$.	k.
1	10^{-3}			0·29±0·03
2	$<10^{-6}$	0·0773	0·00334	0·26±0·03

TABLE III.

Association of cyclo*Pentadiene at 25°. Influence of Acetonitrile.*

Solvent.	CCl_4+MeCN (soltn. contained 10% of MeCN by vol.).	MeCN.	
a	1·615	1·210	2·256
$k \times 10^5$	7·3±2	5·5±0·8	4·7±0·8

TABLE IV.

Association of cyclo*Pentadiene in Carbon Tetrachloride. Influence of Temperature.*

Temp.	0°	22°	35°	55°
a	2·940	3·010	0·9169	1·035
$k \times 10^5$	0·54	5·3	17	100

In Nos. 1 and 2 of Table I and in No. 1 of Table II the solvents were saturated with air and the oxygen concentrations were deduced from the data given by Horiuti (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1931, **12**, 222). In Nos. 3, 4, and 5 of Table I and in No. 2 of Table II the solvents and the reactants were carefully freed from oxygen and mixed without coming in contact with air. Expts. Nos. 6 and 7 of Table I were done without special precaution as described in Part IV (*loc. cit.*). At the end of Expts. 1 and 2 of Table I the Kharasch test (*J. Amer. Chem. Soc.*, 1933, **55**, 2468) was positive, whereas in Nos. 3, 4, and 5 it was negative.

The bromine consumption of *cyclo*pentadiene and di*cyclo*pentadiene in carbon tetrachloride solution has been determined under various conditions. The results are in Table V.

TABLE V.

MeCN, % by vol., in soltn.	0	5	10	20	0	5	10	20
No. of Br atoms used by 1 mol. of *cyclo*pentadiene	1·83—2·07	2·61	2·16	2·21				
No. of Br atoms used by 1 mol. of di*cyclo*pentadiene					2·16—2·66	2·84	2·54	2·72

It was of interest to compare the velocity coefficients of Tables I and III with values deduced from bromine titrations at 25°.. Data for two typical experiments are given in Table VI; the velocity coefficients in the last column were calculated by using equation (7).

TABLE VI.

MeCN, % by vol., in soltn.	Initial concn. of C_5H_6.	t, mins.	$k \times 10^5$.	MeCN, % by vol., in soltn.	Initial concn. of C_5H_6.	t, mins.	$k \times 10^5$.
0	0·996	4000	32	5	0·0300	1325	2370
		10000	10			2560	1290
		14300	8			6850	370
		20200	1300				

The results of the kinetic measurements in the pure liquid state are in Table VII. The initial substance was pure liquid *cyclo*pentadiene in the first three runs and a solution of it in di*cyclo*pentadiene in the other experiments. In No. 4 the di*cyclo*pentadiene was carefully purified, and in No. 5 it contained a relatively large amount of peroxide. The accuracy of the velocity coefficients was 5—7%.

TABLE VII.

Association of cyclo*Pentadiene in the Pure Liquid State.*

No.	Temp.	Initial concn. of C_5H_6.	t, mins.	$k \times 10^5$.
1	− 2°	12·6	2895	0·39
			6960	0·41
			14460	0·38
			25700	0·40
			51870	0·44
2	20	12·1	880	2·8
			2890	3·9
			4430	4·2
			6170	4·9
3	35°	11·7	172	12
			405	13
			1043	16
			1555	16
			2620	19
4		1·155	1329	42
			2891	38
			21600	38
5			1331	40
			2890	40
			21600	40

Hammick and Langrish (J., 1937, 797) made experiments in connexion with the rate of association of *cyclo*pentadiene in carbon tetrachloride at 25° and obtained the results given in Table VIII. The conversion ratios, *C*, in the last column, give the percentage of *cyclo*pentadiene which had been converted at the end of each experiment; the calculation has been carried out by using the figures in cols. 4 and 5 and the mean value of the velocity coefficients of Tables I and III.

TABLE VIII.

No.	Solvent.	MeCN, % by vol., in soltn.	Initial concn. of C_5H_6.	Total time of expt., mins.	$k \times 10^5$.	Kharasch test.	C, %.
1	CCl_4	0	0·0522	1440	Immeasurably small	—	0·6
2		0	0·0522	4200	30	+	2
3		0	0·02976	4080	370	+	1
4	CCl_4 + MeCN	1	0·02976	10140	160		2
5		5	0·02976	8400	140		0·8
6		20	0·03385	10080	90		3
7	MeCN	100	0·00872	11500	Immeasurably small		0·8

The most important results for the kinetics of pure liquid *cyclo*pentadiene obtained by the workers mentioned on p. 381 are summarised in Table IX. The velocity coefficients in col. 4 were obtained by using equation (2) and those in col. 5 by extrapolating the k values to $t = 0$.

TABLE IX.

Association of cyclo*Pentadiene in the Pure Liquid State.*

No.	Temp.	t, mins.	$k \times 10^5$.	$k_0 \times 10^5$.	Workers.	Vel. coeffs. calc. by
1	12°	7200	1·9	1·5	B. and B.	Present authors.*
		14400	2·3			
		21600	2·6			
		28800	3·3 †			
2	20	1440	3·3	3·0	S. and R.	Present authors.*
		3030	3·7			
		4470	4·0			
		5610	4·7			
3	39·4	53	16	16	H., K., and M.	
		120	22			
		191	23			
		438	24			
		1154	35			
4	0	—	—	0·24	H., K., and M.	
	40	—	—	17		
	45	—	—	21		
	58	—	—	78		
	60	—	—	63		
	80	—	—	300		

* Cf. Khambata and Wassermann, *Nature*, 1936, **138**, 368.

† This value corresponds to 90% reaction; the data for still higher conversion ratios have not been taken into account because they are not sufficiently accurate.

DISCUSSION.

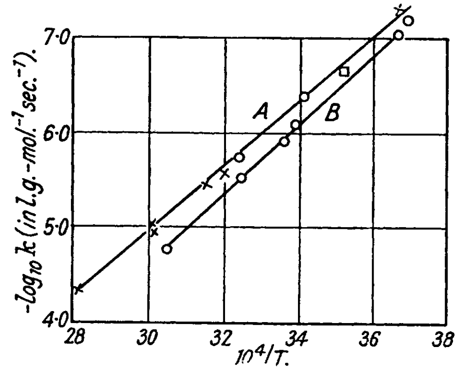
The data in Tables I and III show that the kinetics of the association of *cyclo*pentadiene in carbon tetrachloride solution are not measurably changed by the presence of oxygen, peroxides, or acetonitrile. In pure acetonitrile the rate is smaller but the difference amounts only to about 40%. The experiments of Table II show also that the formation of *cyclo*pentadienebenzoquinone is not influenced by oxygen. This is of interest because the k values of the Tables I, III, IV, and VII have been determined by using the analytical method based on reaction (3).

Hammick and Langrish (*loc. cit.*) attempted to measure the kinetics of the association of *cyclo*pentadiene by a method based on the bromination of *cyclo*pentadiene and di*cyclo*pentadiene. They calculated the k values of Table VIII from an equation which can be written in the form of (7), and concluded that the association of *cyclo*pentadiene is catalysed by peroxides and that the rate is diminished by the progressive addition of acetonitrile, becoming immeasurably small in pure acetonitrile. These conclusions, however, are not justified (cf. p. 387). The data of Table V show that the numbers of bromine atoms used by one mol. of *cyclo*pentadiene and di*cyclo*pentadiene are not equal, which is probably due to the fact that traces of oxygen or peroxides influence the course of the bromination reactions (4) and (5) (cf. Schultze, *loc. cit.*). Further, it is possible that the bromine consumption of *cyclo*pentadiene at zero time does not equal that at time t, and it is not surprising, therefore, that some of the k values in Tables VI and VIII are much larger than the velocity coefficients of Tables I and III, although the conversion ratios in Table VIII are only of the order of magnitude of the experimental error. Thus the k values which are determined by carrying out titrations with bromine cannot relate to the formation of di*cyclo*pentadiene.

The association of *cyclo*pentadiene in carbon tetrachloride is of the second order at all temperatures. In the pure liquid state, on the other hand, the second-order velocity coefficients are constant at — 2°, but they increase at 12°, 20°, 35°, and 39·4° (cf. Tables VII and IX). Catalysis by oxygen, peroxides, or accidental impurities cannot be responsible for the increasing k values; this follows from measurements in the presence of air, carbon dioxide, and di*cyclo*pentadiene peroxide (cf. Stobbe and Reuss, *loc. cit.*, and Expts. 4 and 5 of Table VII), and from determinations which have been carried out in different countries and by using different analytical methods (cf. experiments Nos. 2 of Tables VII and IX). Kistiakowsky *et al.* (*loc. cit.*) assume that the increase of the second-order velocity coefficients is due to the fact that even below 100° not only the formation of di*cyclo*pentadiene but also consecutive reactions have to be taken into account. This, however, is in disagreement with the experiments discussed in Part VI of this series (this vol., p. **366**), which show that, below 100°, the stoicheiometric equation of the non-catalysed thermal reaction is given by (1).

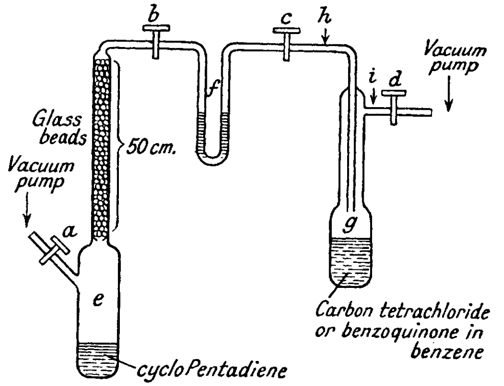
At the early stage of the reaction in the pure liquid state the " solvent " is *cyclo*pentadiene and at the end of the runs it is di*cyclo*pentadiene. The temperature dependence of the reaction order can be explained if it is assumed that above 12° di*cyclo*pentadiene is a " faster " solvent than *cyclo*pentadiene, whereas at — 2° the difference between the velocity coefficients in these two solvents is smaller than the experimental error. Hence the velocity coefficients relating to *cyclo*pentadiene solution should be obtained by extrapolating the observed k values to zero time. In Fig. 1 the logarithms of the velocity coefficients in carbon tetrachloride solution (cf. Table IV) and of the extrapolated velocity coefficients of the associations in the pure liquid state are plotted against the reciprocal absolute temperature. It will be seen that the Arrhenius equation (cf. this vol., p. 362) is obeyed. The non-exponential factors, A (in l. g.-mol.$^{-1}$ sec.$^{-1}$), and the activation energies, E (in kg.-cals.),

FIG. 1.



A = *Pure liquid state* : ☐ = *Vapour pressure measurement.* + = *Refractometric measurement.* ○ = *Benzoquinone method.* B = *Carbon tetrachloride.*

FIG. 2.



	$\log_{10} A$.	E.
In carbon tetrachloride	6·7 ± 0·3	17·1 ± 0·4
Pure liquid *cyclo*pentadiene	5·8 ± 0·5	16·2 ± 0·8

are given above; they are about 10^6 l./g.-mol.-sec. and 16—17 kg.-cals. respectively. The A and E values for the association of gaseous *cyclo*pentadiene, which is known to be a bimolecular process, are similar, and hence it can be concluded that the mechanism of the association of *cyclo*pentadiene in carbon tetrachloride and in the pure liquid state is also bimolecular.

EXPERIMENTAL.

*cyclo*Pentadiene, di*cyclo*pentadiene, and benzoquinone were purified as described in the preceding communications, the bromine was purified by the method of Hammick and Langrish (*loc. cit.*), and the benzene, carbon tetrachloride, and acetonitrile were the purest commercial samples. For some experiments the carbon tetrachloride was purified by fractional crystallisation and subsequent distillation in an all-glass apparatus, but this had no influence on the rate measurements or on the amount of bromine consumed by *cyclo*pentadiene and di*cyclo*pentadiene solutions. The acetonitrile had no measurable bromine consumption. A stream of carefully dried air was passed for 4—5 days through the solvents used for experiments 1 and 2 of Table I and experiment 1 of Table II. The measurements at — 2° were carried out in the thermostat mentioned in Part VIII (this vol., p. 374). The reaction vessels were either sealed glass tubes or ground-stoppered flasks, the joints of which were mercury-sealed.

Experiments 3, 4, and 5 of Table I were carried out in the apparatus shown in Fig. 2. The vessels e and g containing *cyclo*pentadiene and carbon tetrachloride were evacuated for several hours to at least 10^{-2} mm., the four taps were closed, the vessels were warmed, cooled, and evacuated once more. Then the taps *a* and *c* were closed, the *cyclo*pentadiene was slowly distilled into the graduated tube *f*, tap *b* was closed, and the volume of the *cyclo*pentadiene in *f* was determined at 0°. Tap *d*, which was connected with the vacuum pump, was now closed, tap *c* opened, and the *cyclo*pentadiene distilled from *f* into *g*, which was immediately sealed off at *h* and *i*, the vacuum in *g* after sealing being tested with a Tesla coil. The volumes of the *cyclo*pentadiene, as measured in *f*, and of the carbon tetrachloride are given in cols. 2 and 3 of the following table. During the times given in col. 4, vessel *g* was kept in a thermostat, then it was opened, and the volume given in col. 5 was pipetted on an excess of benzoquinone in a 10·0 cm.³ measuring flask. The subsequent determination of $a - x$ was carried out as described in Part IV (*loc. cit.*). The concentration at zero time, *a* (in g.-mol./l.), was calculated from the data in cols. 2 and 3, from the density of *cyclo*pentadiene (cf. v. Auwers, *Ber.*, 1912, **45**, 3078), and from the densities of solutions which were prepared by mixing the required volumes of *cyclo*pentadiene and carbon tetrachloride.

Association of cyclo*Pentadiene in Carbon Tetrachloride: Vacuum Experiments.*

No. of expt. in Table I.	Vol. (cm.³).		t, mins.	Reaction mixture pipetted (cm.³).	Concn. of $C_6H_4O_2$.		$a - x$.
	C_5H_6 at 0°.	CCl_4 at 25°.			Before reaction with C_5H_6.	After reaction with C_5H_6.	
3	1·10	10·0	8617	0·500	0·0400	0·0061	0·678
4	1·51	10·0	7115	0·500	0·0600	0·0284	0·632
5	4·20	10·0	1665	1·00	0·300	0·0610	2·39

In one experiment the concentration of *cyclo*pentadiene at zero time was also determined by mixing the solution with an excess of benzoquinone and by estimating the benzoquinone which had not reacted. The results obtained by the two methods agreed, and it follows, therefore, that no measurable amount of *cyclo*pentadiene remains in the grease of tap *c*.

Experiment No. 1 of Table II was done as described in Part I (*loc. cit.*); in carrying out experiment 2, *cyclo*pentadiene was introduced into vessel *e* of the apparatus represented in Fig. 2, and 85·0 cm.³ of a 0·00335M-solution of benzoquinone in benzene were introduced into vessel *g*. Oxygen and peroxide were removed as described above, and the reaction mixture was prepared by distilling 0·530 cm.³ of *cyclo*pentadiene (0°) from the graduated tube *f* into vessel *g*, which was sealed off and kept for 97 minutes at 14°; the benzoquinone concentration was then 0·00046 g.-mol./l.

TABLE X.

Typical Experiments in Carbon Tetrachloride and in Acetonitrile Solution.

Solvents: Nos. 1 and 2 = CCl_4; No. 3 = MeCN. Temp.: No. 1, 22°; No. 2, 55°; No. 3, 25°. Initial concns. (g.-mol./l.): No. 1, 3·010; No. 2, 1·035; No. 3, 2·256.

(1) t, mins.	6985	8580	10145	12740	17355	28800
$a - x$	1·46	1·28	1·12	1·02	0·80	0·52
$k \times 10^5$	5·3	5·2	5·5	5·1	5·3	5·5
(2) t, mins.	290	340	740	750	1575	7315
$a - x$	0·725	0·751	0·546	0·578	0·370	0·122
$k \times 10^5$	110	103	105	102	105	100
(3) t, mins.	2924	8733	21600	47500	—	—
$a - x$	1·69	1·18	0·698	0·392	—	—
$k \times 10^5$	5·0	4·6	4·6	4·4		

The bromine consumption of *cyclo*pentadiene and di*cyclo*pentadiene in carbon tetrachloride solution was determined by adding an excess of bromine also in carbon tetrachloride, and estimating the excess as described by Hammick and Langrish (*loc. cit.*). The titrations were carried out immediately after the mixing, at room temperature and in diffuse daylight. In typical experiments: (i) 8·62 cm.³ of a 0·1N-bromine solution were added to 10·0 cm.³ of a 0·0300M-solution of *cyclo*pentadiene; 5·53 cm.³ of the bromine solution were used. (ii) A 5·48M-di*cyclo*pentadiene solution was kept for 3 months in a ground-stoppered flask at room temperature; then the solution was diluted 100-fold, and 5·00 cm.³ of the diluted solution were mixed with 0·26 cm.³ of acetonitrile. 11·44 Cm.³ of 0·1N-bromine solution were added to the mixture, and 7·78 cm.³ were used. In order to calculate " velocity coefficients " from equation (**7**), six runs in carbon tetrachloride solution were carried out at 25·0°. In a typical experiment, a 0·996M-solution of *cyclo*pentadiene was sealed in five tubes which were simultaneously introduced into the thermostat. At t = 0, 4000, 9830, 14175, and 20120 mins. the tubes were opened, and the contents diluted 10-fold. 12·00 Cm.³ of 0·1N-bromine solution were added to 5·00 cm.³ of the diluted solution, and 9·95, 7·9, 4·6, 7·4, and 7·1 cm.³ of the bromine solution were used.

In carrying out experiments 1, 2, 6, and 7 of Table I and the experiments of the Tables III, IV, and VII, 0·3—2·0 cm.³ of the reaction mixture were pipetted on an excess of benzoquinone in a 10·0-cm.³ measuring flask; the subsequent procedure was the same as that described in Part IV (*loc. cit.*).

TABLE XI.

Typical Experiments in the Pure Liquid State.

t, mins.	Reaction mixture pipetted in 10 cm.³ measuring flask (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.	Concn. of C_5H_6 in reaction mixture.	t, mins.	Reaction mixture pipetted in 10 cm.³ measuring flask (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.	Concn. of C_5H_6 in reaction mixture.
	Temperature, — 2°.					Temperature, 35°.			
0	0·300	0·545	0·163	12·6	0	0·300	0·397	0·0465	11·7
2895	0·400	0·537	0·0966	11·0	172	0·300	0·397	0·114	9·43
6960	0·500	0·507	0·0443	9·26	405	0·400	0·397	0·108	7·22
14460	0·600	0·515	0·0704	7·42	1043	0·450	0·397	0·221	3·91
25700	0·605	0·376	0·0368	5·60	1555	0·500	0·397	0·248	2·96
51870	0·500	0·276	0·116	3·27	2620	0·500	0·282	0·197	1·71

The *cyclo*pentadiene concentrations at zero time were also deduced from density determinations and the same values as those in Table XI were obtained.

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