81. *The Mechanism of Additions to Double Bonds. Part VI. Kinetics of Gaseous Associations.*

By G. A. Benford and Albert Wassermann.

A study of the kinetics of the formation of gaseous *endo*di*cyclo*pentadiene between 79° and 150°, at initial pressures between 154 and 735 mm., confirms the impression given by previous work, *viz.*, that the gaseous associations known as diene syntheses are characterised by steric factors much smaller than unity. A qualitative explanation for this is suggested.

The non-exponential factor in the Arrhenius equation for the velocity coefficient of a bimolecular reaction can be represented as a product of a steric factor P and a collision frequency Z, and thus we have

$$k = Ae^{-E/RT} = PZe^{-E/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where k is the velocity coefficient and E the activation energy. For gaseous reactions involving atoms or diatomic molecules the steric factor is about unity, and the kinetic A value and the collision frequency are approximately equal. Previous work (see the references in Parts IV and V; J., 1936, 1028; *Trans. Faraday Soc.*, 1938, **34**, 128) makes it very probable that the steric factor of gaseous associations of the type

$$2 \text{ polyatomic molecules} \longrightarrow \text{product} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is much smaller than unity, but further measurements were necessary because in no case had the stoicheiometric equation been established under the conditions of the kinetic measurements. Experiments are now described from which it is possible to deduce not only the rate of an association of the above type, but also the stoicheiometric equation at the highest temperature and at the highest pressure at which kinetic measurements were carried out.

Table I.

No.	Reactants.	Temp. range of kinetic measurements.	Range of initial pressure (mm.).	Ref.
(I)	Acetylene	400—650°	24—2300	1, 2
(II)	Ethylene	315—620	760—200,000	2, 3, 4
(III)	Propylene	330—400	50,000—180,000	4
(IV)	*iso*Butylene	330—370	70,000—200,000	4
(V)	Δ^{2}-Butylene	330—380	70,000—220,000	4
(VI)	Amylene	350—420	120,000—150,000	4
(VII)	Isoprene	255—371	212—739	5
(VIII)	$\Delta^{1:3}$-Pentadiene	279—419	Not given	6
(IX)	2 : 3-Dimethyl-$\Delta^{1:3}$-butadiene	309—400		6
(X)	$\Delta^{1:3}$-Butadiene	326—436	1·5—720	7
(XI)	Acraldehyde and *cyclo*pentadiene	107—209	42—328	8
(XII)	Acraldehyde and isoprene	218—333	39—432	8
(XIII)	Acraldehyde and $\Delta^{1:3}$-butadiene	155—332	43—470	8
(XIV)	Crotonaldehyde and $\Delta^{1:3}$-butadiene	242—300	91—440	8

Table II.

Reaction No.	Products.	Temp.	Press. (mm.).	Phase.	Ref.
(X)	1-Vinyl-Δ^{3}-*cyclo*hexene	100°	760	Gas	6
(XI)	2 : 5-*endo*Methylene-Δ^{3}-tetrahydrobenzaldehyde	<40	760	Liquid	9
(XII)	3(?4)-Methyl-Δ^{3}-tetrahydrobenzaldehyde	100	>760		10
(XIII)	Δ^{3}-Tetrahydrobenzaldehyde	100			11
(XIV)	6-Methyl-Δ^{3}-tetrahydrobenzaldehyde	150			12

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[1] Pease, *J. Amer. Chem. Soc.*, 1929, **51**, 3470; Brunner and Schläpfer, *Helv. Chim. Acta*, 1930, **13**, 1125; Taylor and Hook, *J. Physical Chem.*, 1935, **39**, 811. [2] Travers, *Trans. Faraday Soc.*, 1936, **32**, 236; 1937, **33**, 1345. [3] Pease, *J. Amer. Chem. Soc.*, 1930, **52**, 1158; 1931, **53**, 613; Storch, *ibid.*, 1934, **56**, 374; Russel and Hottel, *Ind. Eng. Chem.*, 1938, **30**, 183. [4] Krause, Nemcov, and Soskina, *Compt. rend.*, *Acad. Sci. U.S.S.R.*, 1934, **2**, 305; **3**, 265; *J. Gen. Chem. U.S.S.R.*, 1935, **5**, 343, 356, 382; Muetzenhaendler, *ibid.*, 1937, **7**, 1848. [5] Vaughan, *J. Amer. Chem. Soc.*, 1933, **55**, 4109. [6] Harkness, Kistiakowsky, and Mears, *J. Chem. Physics*, 1937, **5**, 682. [7] Vaughan, *J. Amer. Chem. Soc.*, 1932, **54**, 386. [8] Kistiakowsky and Lacher, *ibid.*, 1936, **58**, 123. [9] Alder and Stein, *Annalen*, 1934, **514**, 197. [10] Diels and Alder, *ibid.*, 1929, **470**, 85. [11] *Idem*, *ibid.*, 1928, **460**, 121. [12] *Idem*, *ibid.*, 1929, **470**, 87; here and in [11] the approximate yield is not given. We were, however, informed in a private communication that the yield is satisfactory, and hence we conclude that at least 50% conversion takes place.

Previous Work.—The thermal gaseous polymerisations of Table I, which are numbered for further reference, are discussed because the rate-determining step is possibly an association of the type given in equation (2), and it is of interest to decide in which cases the order of magnitude of the steric factor can be estimated. So far as we are aware, the list is complete, but no photochemical polymerisations have been considered.

Reactions (I)—(IX). These are either possibly heterogeneous or influenced by traces of catalysts, and the products are mixtures of compounds of unknown constitution which in some cases depend on the temperature of the kinetic experiments. For these reasons we think that reliable values for the steric factor of bimolecular intermediate reactions cannot be deduced.

Reactions (X)—(XIV). These will be discussed later; they are homogeneous, traces of catalysts do not seem to influence the kinetics, and products of known chemical constitution are formed. In Table II are the names of these products (for formulæ, see Parts IV and V, *loc. cit.*) and the experimental conditions under which at least 50% conversion takes place.

As the experimental conditions to which Tables I and II relate are not the same, the products of Nos. (IX)—(XIV) have also been isolated in the temperature and pressure range of the kinetic measurements (compare ref. 8), but the yields, which were probably very small, have not been determined.

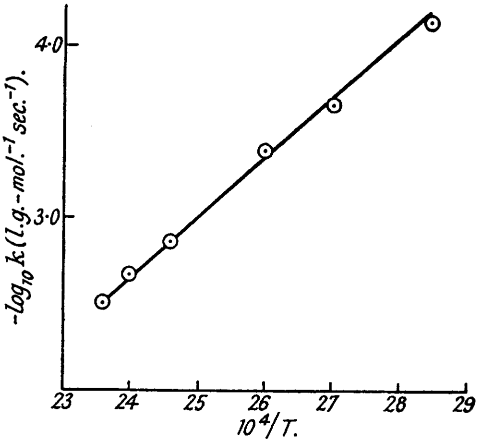
The Association of Gaseous cyclo*Pentadiene.*—We have studied the kinetics of the thermal polymerisation of gaseous *cyclo*pentadiene between 79° and 150° at pressures between 154 and 735 mm. The stoicheiometric equation, determined at 150° and 735 mm., is given by

(XV) 2 *cyclo*pentadiene ⟶ *endo*di*cyclo*pentadiene *

It can be assumed that at lower temperatures and pressures this polymerisation is represented by the same stoicheiometric equation because, at temperatures up to 100°, *endo*di*cyclo*pentadiene is the only product of the polymerisation of liquid *cyclo*pentadiene.

The rate measurements were carried out at constant volume by following the pressure decrease, and it was found that reaction (XV) is homogeneous, of the second order, and that oxygen even in relatively large concentrations does not influence the kinetics. It can, therefore, be concluded that free radicals or peroxidic intermediates play no part, and that the mechanism is bimolecular. The results of the kinetic measurements are in Table III and in Fig. 1. The conversion ratios, *C*, give the percentage of *cyclo*pentadiene which has been converted at the end of each experiment. In the packed vessels the surface/volume ratio was about five times larger than in the unpacked vessels. The coefficient *k* is given in the units l. g.-mol. min.$^{-1}$.

FIG. 1.



The rate of polymerisation of gaseous *cyclo*pentadiene has also been studied by Harkness, Kistiakowsky, and Mears (*loc. cit.*) at 121—192° and at initial pressures between 373 and 1880 mm., and by Schultze (*Oel u. Kohle,* 1938, No. 6, 113) at 132—182° and at initial pressures between 180 and 510 mm. Probably *endo*di*cyclo*pentadiene is not the only product of the polymerisation at pressures above 1 atm. or at temperatures higher than 150°. Hence, it is doubtful whether all the velocity coefficients of Harkness, Kistiakowsky, and Mears relate to reaction (XV). The *A* factors (in l. g.-mol.$^{-1}$ sec.$^{-1}$) and the activation

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* For configuration and constitution of this compound, see Alder and Stein, *Annalen*, 1932, **496**, 232; 1933, **504**, 238; *Angew. Chem.*, 1934, **47**, 837.

energies (E) as deduced from the three sets of kinetic measurements are given in Table IV.

TABLE III.

No.	Temp.	Initial press. (mm.).	C, %.	$-\log_{10} k$.	Conditions.*
1	150°	735	50	0·77+0·03	P
2		735	56	0·75±0·03	E
3		400·5	44	0·80±0·03	
4		221·5	35	0·77±0·03	P
5	145	312·8	44	0·85±0·05	E
6	142	322·7	40	0·89±0·05	
7	134·5	732·0	43	1·07±0·01	
8		392·5	41	1·07±0·01	
9		335·8	30	1·09±0·03	
10	132·7	239·3	15	1·16±0·08	
11		239·5	15	1·11±0·03	P
12	112°	694·9	31	1·62±0·02	E †
13		479·5	21	1·61±0·02	P ‡
14	110	719·1	18	1·68±0·01	E
15		325·2	12	1·68±0·01	
16		200·2	12	1·64±0·03	
17		167·8	5	1·68±0·04	
18	95	720·5	16	1·92±0·02	
19		716·5	16	1·92±0·02	P
20		603·5	19	1·96±0·04	E
21		300·0	7	2·00±0·08	P
22	79	318·7	13	2·41±0·08	
23		165·0	15	2·41±0·06	E

* P = packed vessel; E = empty vessel. † 15·1 mm. air. ‡ 57·5 mm. air.

TABLE IV.

$\log_{10} A$.	E (kg.-cals.).	Measurements by
6·1 ± 0·4	16·7 ± 0·6	Authors *
6·8 ± 0·4	16·9 ± 0·5	Schultze
4·9	14·9	H., K., and M.

* These data were published (*Nature*, 1937, **139**, 669) six months before those of Harkness, Kistiakowsky, and Mears.

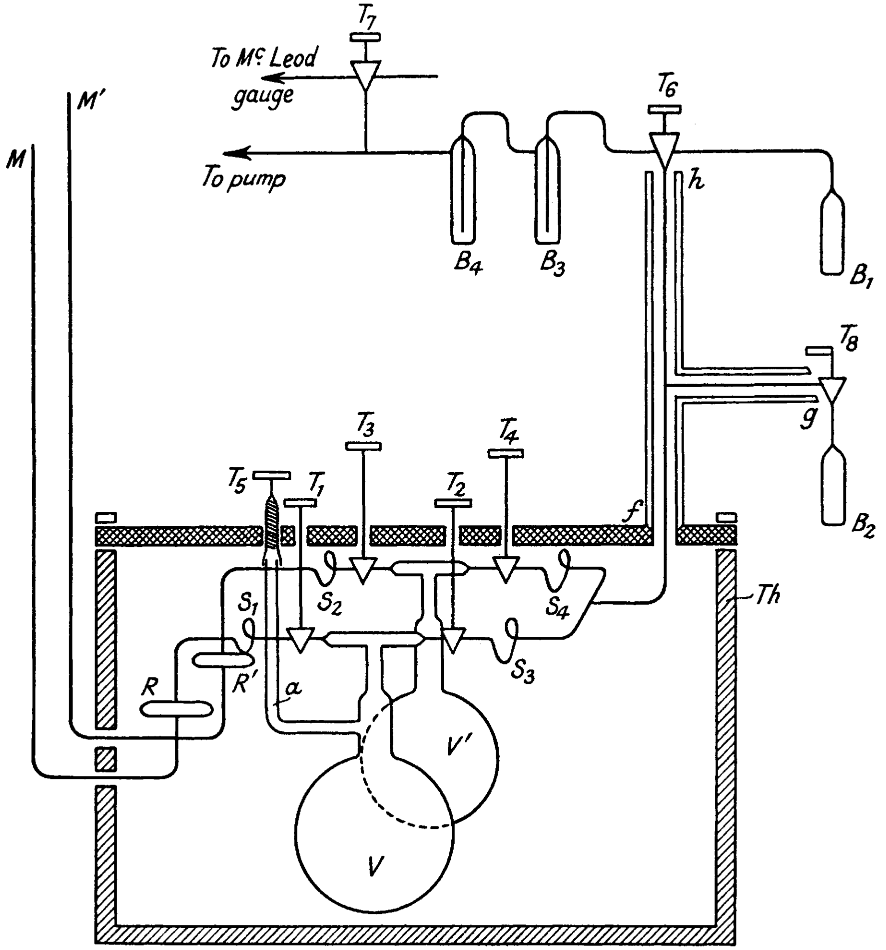
Discussion.—Under the conditions of the kinetic measurements the stoicheiometric equations of the reactions (X)—(XIV) have not been determined, but in view of the facts mentioned on p. 363 it is justifiable to assume that the rate-determining steps are associations of the type given in equation (2), where the reacting molecules and the products are those given in Tables I and II respectively. The velocity coefficients of these associations can be estimated if the observed second-order velocity coefficients are extrapolated to zero time. This procedure is necessary because in each run the velocity coefficients are not constant and the observed increase or decrease is probably due to consecutive and reverse processes. The assumption that the associations are of the second order is justified because at various initial pressures the same values for the extrapolated velocity coefficients are obtained. Furthermore, as measurements at various temperatures have been carried out (see range in Table I), the two parameters of equation (1) can be deduced, and it was found that all the kinetic A factors are of the order 10^6—10^7 l. g.-mol.$^{-1}$ sec.$^{-1}$. The A value of reaction (XV) is of the same order of magnitude (see cols. 1 and 2 of Table IV), and as the collision frequencies are all about 10^{11} l. g.-mol.$^{-1}$ sec.$^{-1}$, it follows from equation (1) that the steric factors are of the order of magnitude 10^{-5}—10^{-4} both for reactions (X)—(XIV) and for (XV).

All these associations are diene syntheses, and the products given in Table II and *endo*di*cyclo*pentadiene can only be formed if two carbon atoms of a double bond add in the 1 : 4-position to a system of two conjugated double bonds. Hence, during a successful collision two polyatomic molecules have to come into contact not at one but at two different and specified positions (cf. Part I, J., 1935, 828; also Guggenheim, *Trans. Faraday Soc.*, 1938, **34**, 144), and the collision must necessarily be unsuccessful if the contact does not occur at the right spots or if one spot only comes into contact. If, on the other hand, bimolecular reactions involving atoms or simple molecules are considered, practically every collision between particles with sufficient energy of the right kind will lead to reaction, and it is, therefore, understandable why, in contrast to the case of diene syntheses, the steric factor is not much smaller than unity.

EXPERIMENTAL.

Apparatus.—This is shown diagrammatically in Fig. 2. The thermostat *Th* was a well-insulated 100-gallon iron tank containing mineral oil which was electrically heated and well stirred. The temperature, measured with standard thermometers both in the thermostat and in the reaction vessel, could be kept constant to within ± 0·1°. The two reaction vessels V and V' were 6-litre Pyrex flasks, and the taps T_1, T_2, T_3, T_4 and T_5 had their keys extended so that they could be operated from outside the thermostat; V was empty and V' contained 100 m. of Pyrex tubing drawn out finely in sections and sealed at the ends. The reaction vessels were connected with the rest of the apparatus through spiral springs, S_1, S_2, S_3, and S_4. It was found that the rate of reaction (XV) is not influenced by gaseous or liquid mercury, and so the pressure measurements were carried out with the mercury manometers M and M'. As the level of the mercury inside the thermostat could not be observed, it was made to lie in the reservoirs R and R', which had a diameter of about 10 cm., so that a large movement of the mercury level in the manometer caused little change in level in the reservoirs and only a small correction was required. T_6 and T_7 were three-way taps, and B_1, B_2, B_3, and B_4 were 100-c.c. bulbs. It was arranged that the part of the apparatus outside the thermostat, from f to g and to h could be maintained at thermostat temperature by winding it closely with metal tubing, the whole being covered thickly with asbestos. Oil from the thermostat was pumped by a rotary pump through the tubing, which was arranged in four sections in parallel. Oil could also be pumped through a well-insulated helical jacket made to fit over the bulb B_2, from which it could be removed when required.

FIG. 2.



Freshly distilled *cyclo*pentadiene was introduced into B_1, and while it was cooled the whole apparatus was evacuated. In order to remove dissolved air or peroxides, about half of the *cyclo*pentadiene was slowly distilled from B_1 to B_2, and while B_2 was cooled the apparatus was evacuated again and then the *cyclo*pentadiene was distilled into the reaction vessels.

The Stoicheiometric Reaction Equation.—Both vessels were filled with *cyclo*pentadiene, the initial pressure being 735 mm. and the temperature 150°. After 290 mins., when the observed pressure was 531 mm., the contents of the vessels were pumped out and condensed into B_3. The product was redistilled, and 9·9 g. (80% of the theoretical amount) of a fraction, b. p. 70·0°/23 mm., m. p. 29—30°, were obtained. A mixture of this with pure *endo*di*cyclo*pentadiene, prepared at room temperature in the liquid phase, had the same m. p. The two samples had also the same Raman spectrum, as can be seen from the following wave numbers (cm.$^{-1}$). The side headings " gas " and " liquid " refer respectively to products which were obtained in the gas phase, at 150°, and in the liquid phase, at room temperature.

Gas	202	319	379	464	—	617	674	—	778	818	912	947	1029	1101	1126
Liquid	205	313	376	465	483	618	675	720	779	817	908	947	1027	1098	1125
Gas	1227	—	1293	1358	1440	1572	1617	2842	2897	2930	2969	3056			
Liquid	1226	1246	1293	1359	1439	1572	1614	2839	2890	2931	2970	3058			

The figures in ll. 2 and 4 are mean values of measurements carried out by Kohlrausch and Seka (*Ber.*, 1936, **69**, 741), Truchet and Chapron (*Compt. rend.*, 1934, **198**, 1934), and Leckie (unpublished), and those in ll. 1 and 3 were determined by Leckie, using the same technique as in previous investigations (cf. J., 1935, 1751).

It was mentioned on p. 363 that below 100° the stoicheiometric equation of the polymerisation of liquid *cyclo*pentadiene is also given by (XV). This follows from measurements by Stobbe and Reuss (*Annalen*, 1912, **391**, 151), Barrett and Burrage (*J. Physical Chem.*, 1933, **37**, 1029), and Kohlrausch and Seka (*loc. cit.*), who found that the refractive index, the vapour pressure, and the Raman spectrum of pure *endo*di*cyclo*pentadiene and of the product of the polymerisation of liquid *cyclo*pentadiene were in agreement. If on the other hand, pure liquid *cyclo*pentadiene is kept at temperatures above 100°, a number of simultaneous consecutive and reverse reactions occur (cf. references on p. 363), and it is therefore probable that the polymerisation of gaseous *cyclo*pentadiene also becomes rather complicated if the temperature is higher than 150° and the pressure is higher than 735 mm.

Kinetics.—In order to show that mercury does not influence the rate, the following experiment was carried out at 150°. The taps T_1 and T_3 were closed, the mercury vapour was pumped from the reaction vessels, and both vessels were filled simultaneously with *cyclo*pentadiene at 735 mm. pressure. In order to determine this pressure, T_1 was opened after T_2 and T_4 had been closed, but T_3 remained closed and the initial pressure in V' was taken as the same as that observed in V. After 76 mins. a pressure of 633 mm. was observed in V, where the *cyclo*pentadiene had been in contact with mercury. Immediately after this reading, T_3 was opened, and it was found that the pressure in V' was almost the same, although here the *cyclo*pentadiene had not been in contact with mercury.

The solubility of *cyclo*pentadiene or di*cyclo*pentadiene in the tap grease does not influence the kinetics. This is proved by the following experiments : (*a*) Taps T_1, T_2, and T_5 were greased with sample (1) of a tap grease and taps T_3 and T_4 were greased with a different sample (2). Both reaction vessels were filled with *cyclo*pentadiene, and the pressure decrease was measured at both manometers : the rates agreed within the limits of the experimental error. (*b*) Tap T_3 was taken away, and the spiral spring S_2 was directly connected with V'. Again, both vessels were filled with *cyclo*pentadiene, and the rate of the reaction determined. No difference could be observed, although in V the gas was in contact with three taps and in V' with only one tap.

The second-order velocity coefficients of Tables III and V have been calculated from

$$k = 125T(P_0 - P_t)/tP_0(2P_t - P_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where T is the absolute temperature, P_0 is the initial pressure in mm., and P_t that observed at time t. The velocity coefficients decrease with increasing time in experiments Nos. 1—6, 10, 11, and 17. It is believed that this is due to the reverse reaction and it is therefore understandable why at 133° and at 110° the decrease was observed only in those runs in which the initial pressure was relatively small. The usual equation for reversible second-order reactions cannot be applied because sufficiently accurate values for the rate constants of the decomposition of di*cyclo*pentadiene are not available. For this reason the velocity coefficients Nos. 1—6, 10, 11, and 17 in Table III were obtained by extrapolating the observed velocity coefficients to zero time. An increase of the velocity coefficients, which is not due to the condensation of the product (cf. below), was only observed in run 12, but here air was present and the increase is probably due to a consecutive reaction between di*cyclo*pentadiene and oxygen (cf. Engler and Frankenstein, *Ber.*, 1901, **34**, 2938); therefore, the velocity coefficient No. 12 in Table III was also obtained by extrapolation to zero time. The rate constants Nos. 7—9, 13—16, and 18—23 in Table III are mean values of the observed velocity coefficients. The data for experiments Nos. 2, 4, 7,and 12 are given in Table V. The time *t* and the pressure *P* are given in minutes and mm. respectively, and the velocity coefficients, *k*, in l. g.-mol.$^{-1}$ min.$^{-1}$.

TABLE V.

No.									
2	*t*	0	10	30	60	76	140	200	285
	P	735	716	685	647	633	584	553	527
	k	—	0·19	0·18	0·18	0·18	0·18	0·17	0·16
4	*t*	0	34	63	94	234	321	405	
	P	221·5	216·5	213·0	209·2	196·9	190·8	185·5	
	k	—	0·17	0·16	0·16	0·15	0·14	0·14	
7	*t*	0	20	40	80	160	320		
	P	732	715	699	672	628	570		
	k	—	0·084	0·086	0·085	0·086	0·086		
12	*t*	0	30	70	139	196	270	350	550
	P	694·9	687·9	679·0	664·0	651·9	637·0	622·9	587·9
	k	—	0·024	0·024	0·024	0·025	0·026	0·026	0·027

Some of the small conversion ratios at the lower temperatures (cf. Table III) are due to the condensation of *endo*di*cyclo*pentadiene, which produces a marked change of the kinetics. In order to obtain reproducible initial rates at 79°, the *cyclo*pentadiene had to be carefully fractionated to remove the last traces of di*cyclo*pentadiene.

The conclusion that reaction (XV) is of the second order is based on the fact that in a number of runs the velocity coefficients remain constant, and that in all cases constant initial velocity coefficients at various initial concentrations are obtained. A comparison of the runs in vessels of large and small surface/volume ratios (see Table III) shows that the reaction is homogeneous. Runs 18 and 19 were done in vessels which had not been used previously, and runs 20 and 21 in vessels in which 20 experiments had previously been carried out. It is not believed that the bulb-to-bulb distillation removed peroxides and oxygen completely, although the distillation was carried out very slowly and the apparatus was evacuated to at least 10^{-3} mm. The statement that peroxides play no part in the reaction is based on the results obtained in runs 12 and 13, in which the rate was not measurably changed although the oxygen concentration was at least 11,000 and 57,000 times larger respectively than in the other experiments.

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