360. *Liquid-phase Reactions at High Pressures. Part V. The Polymerisation of* cyclo*Pentadiene and α-Di*cyclo*pentadiene.*

By B. Raistrick, R. H. Sapiro, and D. M. Newitt.

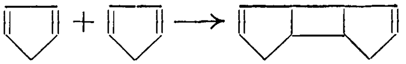
The polymerisation of *cyclo*pentadiene in the pure liquid phase under pressure up to 5000 atm. has been examined at temperatures from 0° to 40°. It was found that the reaction proceeds in three distinct stages, *viz.*, (1) dimerisation to α-di*cyclo*pentadiene only, (2) production of higher polymers, and (3) a violent disruptive reaction, depending upon the temperature and pressure.

The bimolecular velocity constants of the dimerisation reaction have been calculated, experimentally determined compressibility figures being used for correction of the monomer concentration, and the A and E terms of the Arrhenius equation have been derived. Both show an increase with increasing pressure, and reasons for this are discussed. E was found to bear a linear relation to log A.

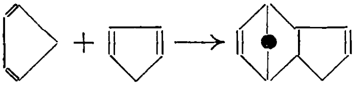
The higher polymers formed in the second stage of the reaction are members of the usual heat-polymerisation series, as are those obtained by subjecting α-di*cyclo*pentadiene to pressure at 138°. In the latter case the results show that polymerisation is dependent upon an initial dissociation into *cyclo*pentadiene.

Very little is known concerning the effect of high pressure upon the kinetics of polymerisations in the liquid phase. Bridgman, Conant, and their collaborators (*Proc. Nat. Acad. Sci.*, 1929, **15**, 680; *J. Amer. Chem. Soc.*, 1930, **52**, 1659; 1932, **54**, 629) investigated the rates of polymerisation of isoprene and *n*-butaldehyde at pressures up to 12,000 atm. In the former case they found the rate to approximate to that of a first-order reaction, and calculated the temperature and pressure coefficients. The results were explained on the basis of a chain mechanism initiated by the decomposition of peroxides to which isoprene is sensitive. Tammann and Pape (*Z. anorg. Chem.*, 1931, **200**, 113) investigated the polymerisation of isoprene, vinyl acetate, styrene, and 2 : 3-dimethylbutadiene at pressures up to 3000 kg./cm.^{2}, and found that the reactions obeyed a unimolecular law. They suggested that the rate was determined by some change undergone by the molecules before combination, and concluded that polymerisation was more favoured by pressure than were other types of reactions. In Part II of this series (J., 1937, 1784) the effect of pressure upon the polymerisation of various aromatic olefins was dealt with, but mainly from the aspect of yields and molecular weight.

Much work has been done on the polymerisation of *cyclo*pentadiene at atmospheric (and lower) pressures in both the liquid and the vapour phase, and also in solution. Various mechanisms have been suggested for the addition of monomer molecules to form the known polymers, notably the schemes (1) and (2) :



(1)



(2)

The first was put forward by Kraemer and Spilker (*Ber.*, 1896, **29**, 552) and supported by

Staudinger and his collaborators (*Helv. Chim. Acta*, 1924, **7**, 23; *Annalen*, 1926, **447**, 97); but the mechanism generally accepted to-day for the heat polymerisation is (2), proposed by Wieland (*Ber.*, 1906, **39**, 1492) and later comprehensively investigated and proved by Alder and Stein (*Annalen*, 1931, **485**, 223; 1932, **496**, 197; 1933, **504**, 205, 216; *Angew. Chem.*, 1934, **47**, 837; 1937, **50**, 510). Early work on the rate of polymerisation was carried out by Étard and Lambert (*Compt. rend.*, 1891, **112**, 945), who followed the progress of dimerisation by measuring the change in density of the reactant. Stobbe and Reuss (*Annalen*, 1912, **391**, 151) examined the reaction in the presence and in the absence of light, in air and in carbon dioxide, at temperatures between −80° and 135°. They concluded that illumination had no appreciable effect upon the rate of polymerisation, and that, whereas only dimerisation took place below 100°, higher polymers were formed at 135°. Barrett and Burrage (*J. Physical Chem.*, 1933, **37**, 1029) studied the reaction by observing the change in vapour pressure of the system, but gave no rate constants. Much work upon the kinetics of the polymerisation has recently been carried out by Wassermann and his collaborators (*Nature*, 1936, **137**, 496; **138**, 368; 1937, **139**, 669; this vol., pp. 362, 870), who have studied the rates of formation and decomposition of di*cyclo*pentadiene in the pure liquid state, in various solvents, and in the gaseous phase. The A and the E term of the Arrhenius equation were calculated and the values discussed from the aspect of statistical mechanics. Kistiakowsky and his collaborators (*J. Amer. Chem. Soc.*, 1936, **58**, 1060; *J. Chem. Physics*, 1937, **5**, 682) also carried out similar investigations. The data and conclusions reached by Wassermann and Kistiakowsky will be referred to in discussing the results of the present paper, which deals with the liquid-phase polymerisation of *cyclo*pentadiene at pressures up to 5000 atm. over a temperature range of 0° to 40°.

In general, we have found that, according to the temperature and pressure conditions, *cyclo*pentadiene under pressure, in the liquid phase, undergoes polymerisation in three distinct stages, *viz.*, (1) dimerisation, where the products are α-di*cyclo*pentadiene and unchanged monomer only; (2) association to higher polymers, amongst which trimer and tetramer have been identified; and (3) an explosive decomposition reaction producing gas and a highly carbonised residue usually enclosed in a thin envelope of horny insoluble material.

The dissociation and polymerisation of α-di*cyclo*pentadiene under pressure at 138° has also been examined and the data obtained are discussed in this paper in conjunction with those for stages (1) and (2) of the polymerisation of *cyclo*pentadiene. Stage (3) is dealt with in the following paper.

EXPERIMENTAL.

(a) *General.*—Two types of pressure apparatus were used. For determining the velocity of dimerisation of *cyclo*pentadiene an assembly giving temperature control to within 0·1° was employed (see J., 1938, 785); it will be referred to as " Apparatus I ". This was also used in determining the pressure–temperature limits of the three polymerisation stages. For investigation of the decomposition of α-di*cyclo*pentadiene, however, an earlier-described assembly (J., 1937, 876) was employed since it permitted the use of larger volumes of reactant and the temperature control available (± 2° at 135°) was sufficiently accurate for the purpose. This is referred to as " Apparatus II ".

(b) *Materials.*—Pure α-di*cyclo*pentadiene as purchased was redistilled under 0·1 mm. The fraction used had b. p. 51°/0·1 mm., m. p. 32—32·5°, $n_D^{35^\circ}$ 1·5050. Kraemer and Spilker (*loc. cit.*) found $n_D^{35^\circ}$ 1·5050, and m. p.'s given in the literature vary from 31° to 32·9°.

*cyclo*Pentadiene was prepared from the purified dimeride by heat depolymerisation in the usual manner with fractionation of the monomer through an efficient column. The distilled monomer was dried over calcium chloride and was then refractionated through a column immediately before use. B. p. and refractive index were used as a check upon each portion used in the experiments. The purified monomer had b. p. 40·0°/760 mm., $n_D^{25^\circ}$ 1·4404, $d_{4^\circ}^{25^\circ}$ 0·7966. [Density figures at other temperatures are given later in the text. The refractive index and density figures agree with those of Kraemer and Spilker (*loc. cit.*), von Auwers (*Ber.*, 1912, **45**, 3077), and Schultze (*J. Amer. Chem. Soc.*, 1934, **56**, 1552), but not with those of Zelinsky and Levina (*Ber.*, 1933, **66**, 477).]

The mercury used to seal the reactant from the pressure-transmitting medium was purified by repeated agitation with solvents, nitric acid, and distilled water, and was dried in a vacuum oven.

(c) *Experimental Method and Analysis.*—The pure monomer, confined over mercury in a stainless-steel tube 7 cm. long and 0·875 cm. in internal diameter (Fig. 2), was allowed 5 mins. to attain the temperature of the reaction vessel before the latter was closed and pressure applied. In rate determinations the time recorded is the interval between the attainment of half the maximum pressure when pressure was applied and released at a uniform steady rate. In the high-temperature experiments in which the velocity of dimerisation is comparatively high it is necessary to pump up to the working pressure as rapidly as possible, due regard being paid to the necessity for maintaining substantially isothermal conditions. A number of tests were carried out with different rates of pumping to determine the maximum permissible rate, and this was found to be about 1500 atm./min. Direct measurements of the temperature of the reactants and pressure-transmitting liquid, immediately after rapid release of pressure from 5000 atm. (in about 1 min.), also showed that substantial thermal equilibrium was established within 1—2 minutes.

FIG. 1.

Polymerisation diagram of cyclo*pentadiene.*

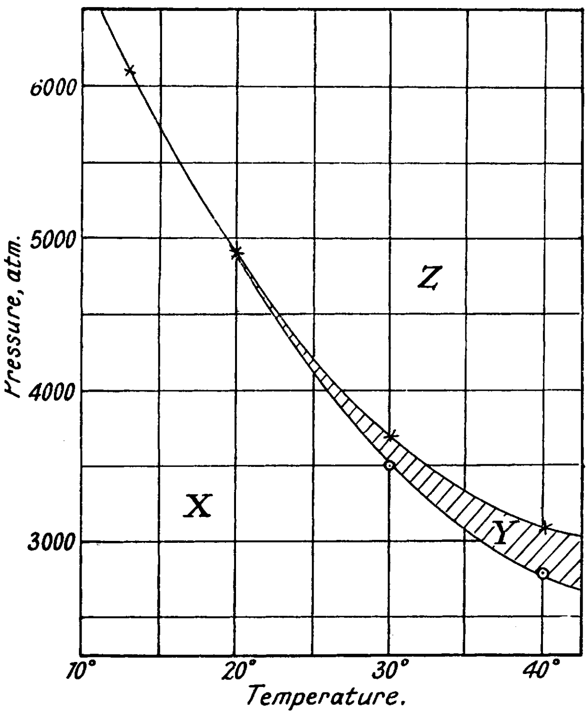
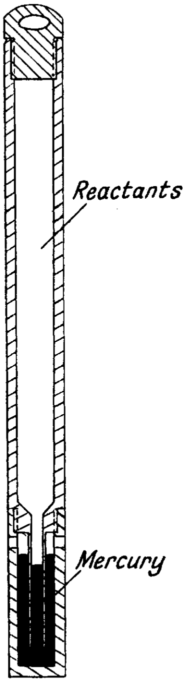


FIG. 2.

Stainless steel reaction tube.



Finally, the experimental data themselves afford an indication that isothermal conditions are maintained save in those experiments in which carbonisation occurs. For example, the velocity constants calculated from the data for short-time runs are in no case higher than those for corresponding long-time runs in which several hours are available for temperature equilibrium to be established.

During the course of an experiment any pressure fall, due to volume decrease as a result of polymerisation, was corrected immediately. This precaution was particularly necessary in the initial stages of any experiment where the rate of polymerisation was comparatively high. After removal from the pressure vessel, the reaction tube was rapidly chilled to 0°, and the product was estimated as described below.

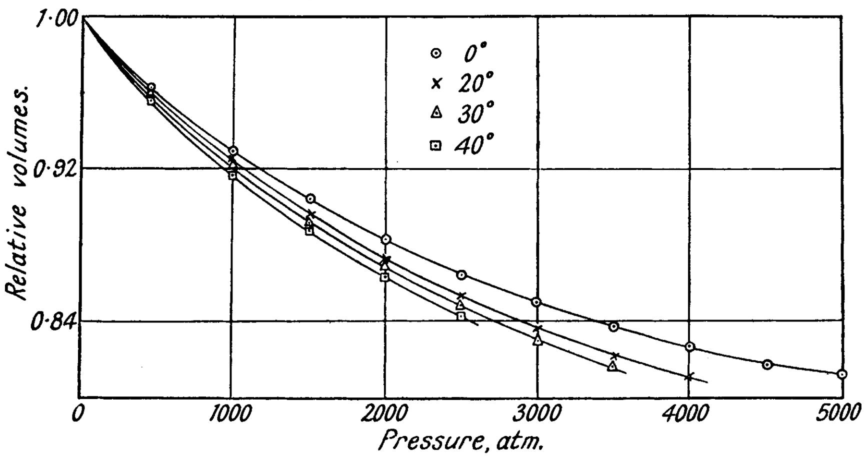
For experiments at atmospheric pressure a larger tube of the same steel was used, and was kept completely immersed in mercury, the whole assembly being maintained at the required temperature in a thermostat. At definite time intervals samples for analysis were withdrawn by means of a fine pipette after the tube had first been chilled to about −40°. Any air space in the tube was then filled with mercury, and the assembly returned to the thermostat.

To determine the pressure–temperature limits of the three stages of polymerisation (Fig. 1) the following procedure was adopted : pressure was applied at a steady uniform rate until a sudden pressure rise, indicating the occurrence of explosive decomposition, was recorded on the Bourdon gauge of the low-pressure side of the intensifier. The experiment was then repeated at diminishing pressure intervals of 100 atm. until carbonisation failed to occur, sufficient time being allowed for any induction, or delay, period. By following this procedure at the different temperatures the boundary between areas *Y* and *Z* (Fig. 1) was obtained with an accuracy of within 100 atm., *Z* being the carbonisation area. In a similar manner the boundary between the dimerisation and higher polymerisation areas, *X* and *Y*, was found with a like degree of accuracy, the limit for *X* being the maximum pressure at which the product of prolonged reaction gave a residue which, after evaporation at room temperature and reduced pressure, had a m. p. of not less than 31°.

The percentage dimerisation in area *X* was estimated by determining the change in refractive index by means of an Abbé refractometer at 25° ± 0·1°, and comparing the result with a reference curve constructed by using weighed mixtures of pure monomer and pure α-di*cyclo*pentadiene. Tests for polymers other than α-di*cyclo*pentadiene were frequently made by the above m. p. test, especially in the products from long-period experiments. The percentages of dimeride estimated thus are probably accurate to 0·5.

FIG. 3.

Compressibility of cyclo*pentadiene.*



To test the effect of peroxide upon the rate of dimerisation, duplicate experiments were performed with monomer alone and with monomer containing (*a*) 0·5 and (*b*) 1·0% by weight of benzoyl peroxide. The experimental conditions were : 4000 atm. and 20°, atmospheric pressure and 20° and 2500 atm. and 40°. Within the limits of experimental error, peroxide was found to have no measurable effect upon the rate. This observation is in agreement with the work of Schultze (*loc. cit.*) on the effect of oxygen and peroxide on the liquid phase polymerisation of *cyclo*pentadiene.

(d) *The Velocity Constants.*—For a full correction of the *a* term (the concentration of *cyclo*pentadiene) of the bimolecular equation $k = (1/at)x/(a - x)$, it is necessary to know (1) the density of *cyclo*pentadiene at the experimental temperature, and (2) its compressibility over the pressure range covered.

Owing to the high volatility of *cyclo*pentadiene, density measurements at atmospheric pressure had to be carried out in a pyknometer so designed as to prevent loss due to evaporation while filling and weighing. The following values were obtained :

Temp.	0·0°	10·0°	20·0°	25·0°	30·0°
$d^{t°}_{4°}$	0·8235	0·8131	0·8021	0·7966	0·7914

$d^{40°}_{4°}$ was found from the above data by graphical extrapolation.

The compressibility isotherms at the four experimental temperatures are reproduced in Fig. 3. The method employed for the measurements, which will be fully described in a later publication, involves the use of a glass tube of known volume, calibrated at each of a series of sealed-in platinum wire contacts. These contacts are connected to a fine resistance wire wound spirally round the tube. The change in volume of the liquid as pressure is progressively applied is recorded by changes in the total electrical resistance of this wire as each successive contact is reached by the rising column of the mercury seal within the tube. The isotherms in Fig. 3 are corrected for the compressibility of glass.

The apparent velocity constants, calculated from the bimolecular equation by using the corrected values of a, show an increase with time, and in order to obtain the true values it is necessary to extrapolate the calculated values of $1/t.\,x/(a - x)$ to zero time. The results are given in Table I, which includes (1) the values of a in g.-mols./l. at atmospheric pressure at the four temperatures, (2) the fractional volume or compressibility correction, (3) the corrected bimolecular velocity constants in l./g.-mol./min., and (4) the values of k_p/k_1.

TABLE I.

Values of the Bimolecular Velocity Constant.

Press. (atm.).	$\frac{x}{t(a - x)}$.*	Fractional volume.	$k \times 10^6$.†	k_p/k_1.	Press. (atm.).	$\frac{x}{t(a - x)}$.*	Fractional volume.	$k \times 10^6$.†	k_p/k_1.
Results at 0·0° : a = 12·47 g.-mols./litre.					Results at 20·0° : a = 12·14 g.-mols./litre.				
1	0·00303	1·000	4·05	—	1	0·0220	1·000	30·2	—
2000	0·0188	0·883	22·2	5·48	1000	0·0740	0·926	94·1	3·12
3000	0·0438	0·850	49·8	12·3	2000	0·193	0·873	231	7·65
4000	0·0870	0·826	96·0	23·7	3000	0·406	0·836	466	15·45
5000	0·165	0·812	179	44·2	4000	0·905	0·811	1007	33·3
Results at 30·0° : a = 11·98 g.-mols./litre.					Results at 40·0° : a = 11·82 g.-mols./litre.				
1	0·0580	1·000	80·7	—	1	0·142	1·000	200	—
1000	0·200	0·922	256	3·17	500	0·303	0·959	410	2·05
2000	0·516	0·869	624	7·74	1000	0·490	0·920	636	3·18
3000	1·29	0·830	1490	18·5	2000	1·44	0·864	1750	8·75
3500	2·06	0·816	2340	29·0	2500	2·40	0·844	2850	14·25

* Extrapolated values : t in hours.

† In units (l./g.-mol.)/min.

In Table II the values of k_p/k_1 for the various pressure intervals are tabulated against temperature, and they show an increase with temperature, particularly in the higher pressure ranges. The values of log k as a function of pressure at the four temperatures are shown in Fig. 4, and as a function of the absolute temperature at the various pressures in Fig. 5. In both cases a series of almost parallel straight lines is obtained from the slopes and intercepts of which the values of the activation energy term E and the collision factor A of the Arrhenius equation have been deduced for the various pressures; these are summarised in Table III.

TABLE II.

The influence of temperature on the ratio k_p/k_1 *for various pressure ranges.*

	Values of k_p/k_1 for the pressure range (atm.) :							
Temp.	1—500.	1—1000.	1—2000.	1—2500.	1—3000.	1—3500.	1—4000.	1—5000.
0°	1·53	2·45	5·48	8·49	12·3	17·3	23·7	44·2
20	1·66	3·12	7·65	10·9	15·5	22·7	33·3	
30	1·86	3·17	7·74	11·8	18·5	29·0		
40	2·05	3·18	8·75	14·25				

TABLE III.

Values of E *and log* A *at pressures up to* 5000 *atm.*

Pressure (atm.)	1	500	1,000	2,000	2,500	3,000	3,500	4,000	5,000
E (cals.)	17,000	17,350	17,650	18,250	18,400	18,600	18,800	18,850 (approx.)	—
$\log_{10}A$, (l./g.-mol.)/min.	8·18	8·70	9·15	9·96	10·28	10·59	10·91	11·1	11·4

(e) *The Higher Polymerisation Area.*—The combined product from two experiments at 3000 atm. and 40° (about 7 c.c.) was fractionated in a vacuum. α-Di*cyclo*pentadiene (yield about 70%) was identified by refractive index, m. p. and mixed m. p. From the distillation residue more dimeride was removed by solution in cold methyl alcohol, and the residue (about 4%) was extracted with boiling methyl alcohol. This solution gave a white solid, m. p. 64°, on cooling. Recrystallisation gave crystals, m. p. 66°, either alone or admixed with authentic α-tri*cyclo*pentadiene. The residue insoluble in hot methyl alcohol probably consisted mainly of tetramer (m. p. 207°). It melted at 120—124° but the amount was too small for further treatment.

(f) *Polymers from α-Di*cyclo*pentadiene.*—The purified starting material, contained in a glass tube over mercury, was subjected to pressure in Apparatus II at a temperature of 138° ∓ 2°. Twelve experiments were carried out, three time periods (21, 44, and 72 hours) and four pressures (1, 2000, 3600, and 5000 atm.) being used. The products obtained under these conditions were

FIG. 4.

Pressure coefficient of log k *at various temperatures.*

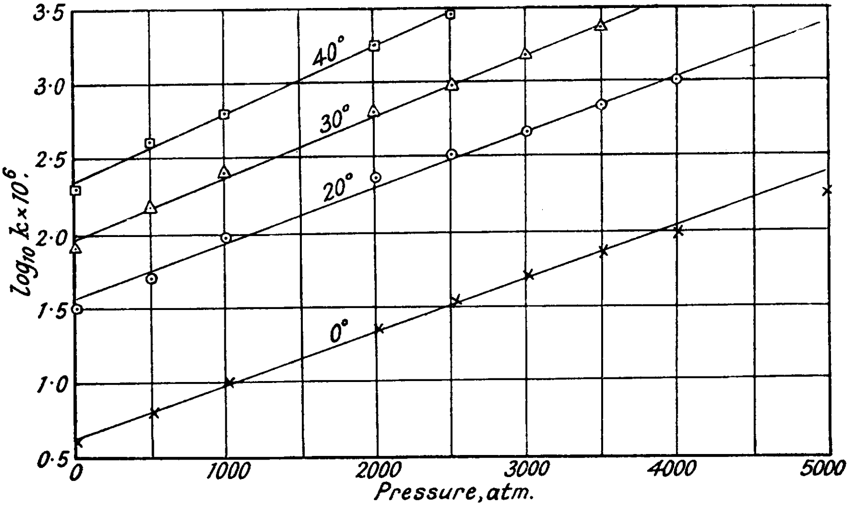
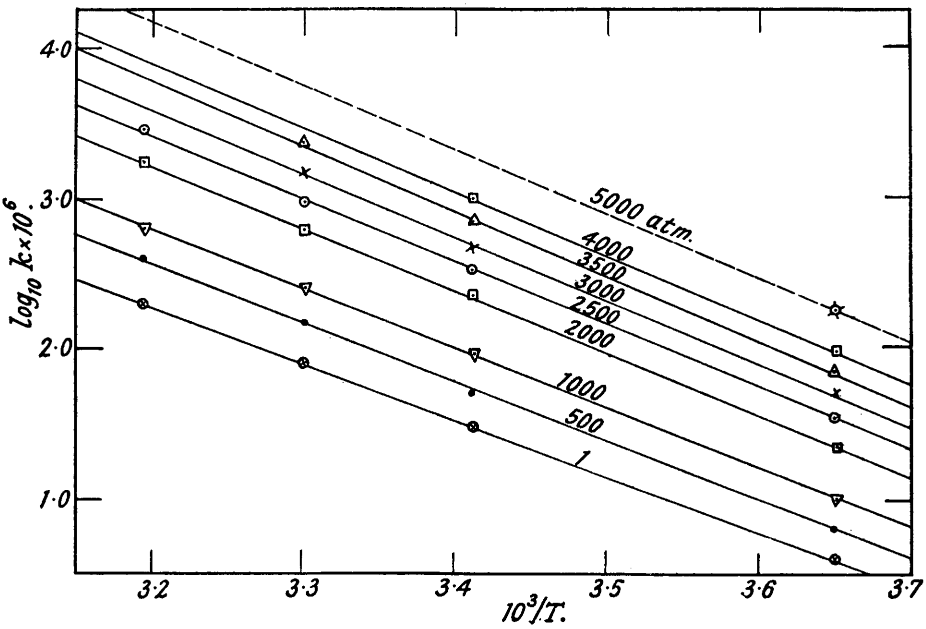


FIG. 5.

Temperature coefficient of log k *at different pressures.*



always liquid at the experimental temperature. About 15 g. of the product were weighed and fractionated at 0·1 mm., and dimer and trimer fractions were thus removed and weighed. The residue was then repeatedly extracted with cold ether to dissolve tetramer, and the insoluble portion was boiled with benzene to remove pentamer. The higher polymer remaining undissolved corresponded with a material called poly*cyclo*pentadiene by Staudinger (*loc. cit.*, 1926), who considered it to be hexamer.

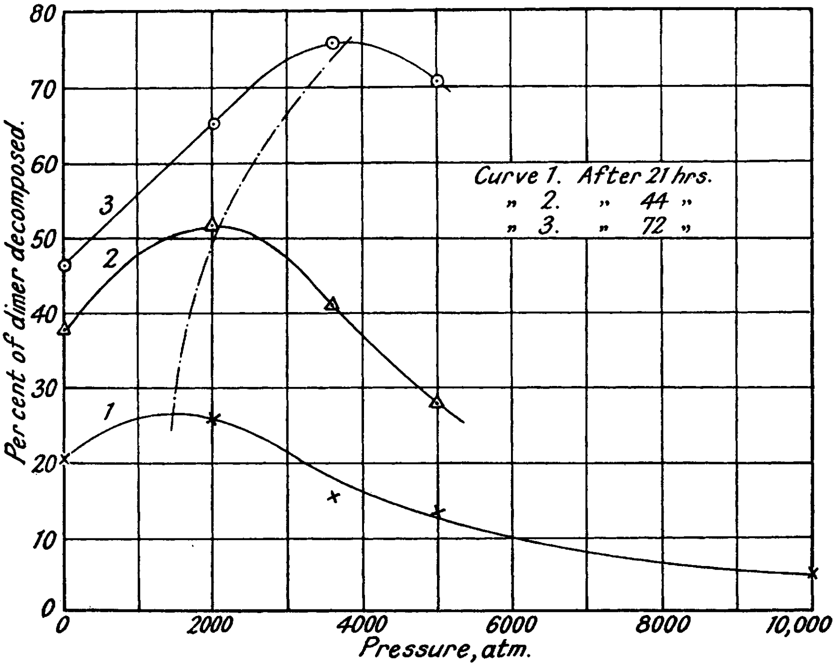
The m. p.'s of the crude fractions were low in all cases, 5—10° in the case of dimer, trimer, and pentamer, and up to 30° in the case of tetramer; but since in most cases each fraction would be contaminated with small amounts of the polymers higher and lower in the series, errors would to a certain extent be balanced. The figures given in Table IV are therefore subject to a small error.

TABLE IV.

Yields of Higher Polymers from α-Dicyclopentadiene at 138° ± 2°.

Pressure (atm.).	Dimer decomp., %.	Trimer formed, %.	Tetramer formed, %.	Pentamer formed, %.	Hexamer formed, %.
		Time = 21 hours.			
1	20·5	16	2	—	—
2,000	26	25	1	—	—
3,600	15·5	14	1	—	—
5,000	13·5	10	1	—	—
10,000	4 or 5	—	—	—	—
		Time = 44 hours.			
1	37·5	23	11·5	0·5	—
2,000	52	27	20·5	1	—
3,600	41	25	12	1	—
5,000	28	17	11	1	—
		Time = 72 hours.			
1	46·5	26·5	15	1·5	—
2,000	65	31·5	28·5	2·5	—
3,600	76	29	39	5	<0·5
5,000	71	22	43	6	<0·5

FIG. 6.



The experiment at 10,000 atm. pressure was carried out in an apparatus of much smaller capacity and the product was too small in amount to be estimated by the above method. The yield was computed on the basis of refractive index change and the molar freezing-point depression constant for α-di*cyclo*pentadiene given by Pirsch (*Ber.*, 1934, **67**, 101), the higher polymer being assumed to be tri*cyclo*pentadiene, though it would undoubtedly contain some higher members of the series. In Fig. 6 the percentage of dimer changed is plotted as a function of the pressure for each of the three trime periods.

When α-tri*cyclo*pentadiene was subjected to the same temperature conditions at atmospheric pressure and also at 3600 atm. it remained quite unchanged, as shown by its m. p. alone or mixed with untreated trimer.

The components of reaction mixtures were identified not only by m. p. but also by the m. p.'s of their phenyl azide addition compounds prepared by the method of Alder and Stein (*loc. cit.*, 1931). Below are the m. p.'s of these derivatives with, in parentheses, those given by Alder and Stein : Phenyl azide addition compound of α-di*cyclo*pentadiene, 129° (128°) ; α-tri*cyclo*pentadiene, 199° (199°) ; tetra*cyclo*pentadiene, 220° (222°) ; penta*cyclo*pentadiene, 258° (—).

DISCUSSION.

(a) *The Dimerisation Area.*—The increase in the bimolecular velocity constants for any given set of temperature and pressure conditions may be due to one of the following causes :

(1) Kistiakowsky and his collaborators (*loc. cit.*, 1937) believed that the increase was only an apparent one due to an error in estimation by the refractive-index method. They suggested that another polymer with a higher refractive index than that of α-di*cyclo*pentadiene was also formed, leading to an over-estimation of the amount of dimer. It may be pointed out that Wassermann and Khambata (*Nature*, 1936, **138**, 368) also noted an increase in the velocity constants when using a colorimetric method of estimating monomer in their determinations. We are satisfied that in the dimerisation area here dealt with no polymer is formed other than α-di*cyclo*pentadiene.

(2) Polymerisation in the pure liquid state may not be a bimolecular reaction.

(3) In the liquid phase, polymerisation starts in pure *cyclo*pentadiene as solvent, continuing in a solvent containing an ever-increasing concentration of dimer. Wassermann and Khambata (*loc. cit.*) suggested that the increased velocity is due to a higher rate of polymerisation in dimer solution than in monomer, though in later work Kaufmann and Wassermann (this vol., p. 870) have shown that the velocity coefficients are not markedly changed by the solvent. Though the density of dimer is greater than that of monomer, and hence monomer concentration is greater at any stage during polymerisation than it would be if the densities of the two hydrocarbons were equal, the increase in velocity found is too great to be explained entirely on this basis.

Examination of the results given in Table II shows a rapid rise of the corrected velocity constant with increase of pressure, the values of k_p at 3000 atm. being more than 10 times greater than the k_1 values for the same temperature. This indicates that the dimerisation belongs to the class of " slow " reactions (see Moelwyn-Hughes, " The Kinetics of Reactions in Solution," Chap. IV, Oxford, 1933), where the velocity constant is usually several powers of 10 smaller than that calculated from the rate of collision (gas-collision equation) and the measured activation energy.

That the pressure effect is dependent upon temperature is shown by the data in Table II. The k_p/k_1 ratio increases with temperature, particularly in the higher pressure ranges.

Regarding the values at atmospheric pressure for the E and A terms of the Arrhenius equation given in Table III, it may be noted that Wassermann (this vol., p. 362) gives 16,000 ± 1000 cals. for E, whereas Kistiakowsky (*loc. cit.*) found 17,000 cals. Also the figure for A at atmospheric pressure given in the table is equivalent to 6·40 if the time unit is seconds. For the same condition Wassermann gives 5·7 ± 0·9, and Kistiakowsky 6·3.

There is an apparent increase in the activation energy with pressure, together with a more than compensating increase in A. The latter term includes the collision number Z and the probability factor P, both of which may vary with pressure. If it is assumed that the collision number is constant at 10^{14}, *i.e.*, is about 10^3 greater than the gas-collision number (Wassermann and Khambata, *loc. cit.*), then it is seen that when pressure is increased from 1 to 5000 atm. the probability of interaction between two molecules with the requisite energy is increased by more than 10^3 times. Although such a result might be unexpected, it is not improbable. The viscosity of the reactant is probably increased by a factor of at least 10 when a pressure of 5000 atm. is applied to it, and the tendency towards orientation of the molecules, always evident in the liquid phase, is thereby increased. A big increase in the probability factor would result on the assumption that such orientation brings pairs of molecules into the correct position for interaction. In Part III (J., 1938, 784) it was shown that, in the esterification of acetic acid with *sec.*-butyl alcohol, where there is an 11-fold viscosity increase over a pressure range of 1 to 3500 atm., the value of P is increased by about 10^4 times. The activation energy term E is composite, and the observed variation with pressure may be due, for example, to a change in the activation energy of diffusion.

Since both A and E contain terms which depend upon changes in certain physical properties of the reactant, some simple relationship between them is to be expected. Thus it is found that log PZ is a linear function of E within the limits of experimental error. The functional relationship between A and E has been discussed by Fairclough and Hinshelwood (J. ,1937, 797), who found that, on certain reasonable assumptions, a linear relationship should hold between log A and $1/\sqrt{E}$.

(b) *The Mixed Polymerisation Area.*—The area Y in Fig. 1 represents temperature–pressure conditions intermediate between dimerisation and a disruptive decomposition reaction. Its width decreases from about 300 atm. at 40° to 200 atm. at 30°, and below 20° no mixed polymer formation occurs. The boundary line between X and Y cuts the temperature axis at about 100°, at which temperature Wassermann and Khambata (*loc. cit.*) observed the formation of *cyclo*pentadiene from dimer, and Staudinger and Bruson (*loc. cit.*, 1926) found that 2% of tri*cyclo*pentadiene was formed from dimer in a period of 2 weeks.

Under the conditions defined by the area Y, mixed polymers are formed rapidly, 30 mins. at 40° and 3000 atm. producing some 6—10% of trimer along with 4% of unchanged monomer, the remainder being dimer.

(c) *The Polymerisation of α-Di*cyclo*pentadiene.*—Most of the earlier work on polymers from α-di*cyclo*pentadiene was carried out by Staudinger and Bruson (*loc. cit.*) and by Alder and Stein (*loc. cit.*). The former authors isolated tri-, tetra-, penta-, and poly-*cyclo*pentadienes formed by the action of heat on α-di*cyclo*pentadiene in sealed glass tubes. The work was semi-quantitative, and the yields of polymers under different temperature conditions were recorded. The proposed structure of dimer and of trimer, according to Alder and Stein, requires that the formation of higher polymers from dimer takes place only after dissociation of part of the dimer to monomer. With the structure suggested by Staudinger, tetramer could be formed by the union of two suitably activated dimer molecules without dissociation occurring. At no time during the present investigation was there any reason to suspect that this was the case.

Examination of the pressure–polymerisation curves in Fig. 6 shows that each curve has a maximum for a certain pressure which shifts towards higher pressure conditions as the time of reaction is prolonged. Table IV also shows that pressure favours the production of higher polymers, especially with prolonged time, *i.e.*, increasing yields of tetramer and pentamer are obtained at the expense of trimer.

Two types of reactions are apparently taking place, (1) dissociation of dimer to monomer, and (2) addition of monomer to monomer, dimer, trimer, etc. Since application of pressure increases the rate of dimerisation and higher polymerisation, it must inhibit (1). The maxima on the curves therefore represent those conditions under which, within a given time period, the inhibition of dissociation of dimer becomes the preponderating pressure effect. Since the resultant effect of increased pressure beyond these maxima is a decreasing total production of polymers, the belief that dimer–dimer addition is not taking place is confirmed. It has already been mentioned that α-tri*cyclo*pentadiene is quite unchanged under pressure at 138°.

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