361. *Liquid-phase Reactions at High Pressures. Part VI. The Explosive Decomposition of* cyclo*Pentadiene.*

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

The carbonisation of *cyclo*pentadiene under pressure has been investigated with regard to the dependence of the carbonisation pressure upon temperature, tube diameter, the material from which the reaction tube is made, and the presence of a diluent. The results are discussed from the point of view of the mechanism of the reaction.

In general, the effect of diluents is a progressive increase in the critical carbonisation pressure with increasing dilution.

The main products, gas and carbonaceous residue, have been examined, and the structure of the latter is discussed.

In Part V (preceding paper) it was mentioned that, under certain conditions of temperature and pressure, *cyclo*pentadiene undergoes an explosive decomposition accompanied by a rapid rise in pressure. This rise may be as much as 2,000 atm. or more, depending upon the experimental conditions and the volume of reactant used. The products are (1) large quantities of gas, and (2) a highly carbonaceous residue usually enclosed in an envelope of semi-transparent insoluble material. In view of the comparative rarity of such reactions in the liquid phase it was thought of interest to investigate this example in some detail.

The reaction takes place under conditions defined by the area *Z* of Fig. 1 (Part V), and is found to be very sensitive to temperature, pressure, the diameter of the reaction tube, and the nature of the material of which the tube is made.

Experimental.

As previously described, the area *Z* was found by using the steel tube shown in Fig. 2 (Part V), the " minimum critical carbonisation pressure " (M.C.C.P.) determined at any temperature being defined as the lowest pressure at which carbonisation would ultimately occur. The values so obtained are given below :

Temp.	13°	20°	30°	40°
M.C.C.P. (atm.)	6100*	4900	3700	3100

* It was not safe to exceed this pressure in search of results at lower temperatures.

The M.C.C.P. is sharply defined and can be measured accurately to within 100 atm.

Factors influencing the Critical Carbonisation Pressure.—(a) *The dimensions of the reaction vessel.* To determine the influence of vessel diameter upon the critical pressure a series of experiments was carried out in Apparatus II (see Part V), soda-glass tubes of constant length but different diameter being used. The internal diameters varied from 23 mm. (the largest which could conveniently be accommodated in the apparatus) to 4·75 mm.

As a matter of convenience, the critical pressure measured (C.C.P.) was not the minimum critical carbonisation pressure, but that pressure at which carbonisation occurs when the pressure is increased at a uniform rate of 1,500 atm. per minute. It does not, therefore, take into account the induction periods preceding carbonisation which may vary from 1 sec. to as much as 74 secs., depending upon the diameter of the tube and other factors.

The results at 20° and 30° (± 0·1°) are summarised in Table I and are shown graphically in the figure.

Table I.

Variation of Critical Carbonisation Pressure with Tube Diameter at 20° and 30°.

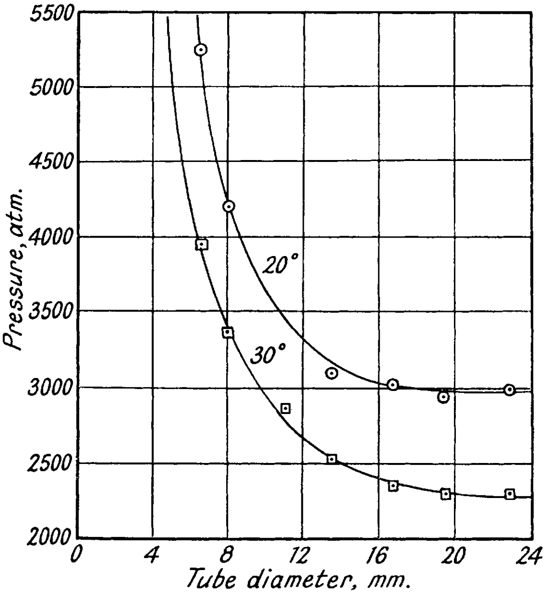
Diameter (mm.)		23	19·5	16·75	13·5	11	8	6·5	4·75
C.C.P. (atm.)	At 20°	3000	2950	3025	3100	3250	4200	5250	—
	At 30°	2300	2300	2350	2525	2875	3375	3950	>5500

Comparable experiments in tubes in which the internal diameter was maintained constant but the length varied showed the C.C.P. to be independent of length.

(b) *The material of the reaction vessel.* The critical pressure was found to depend upon the material of which the reaction vessel was made; *e.g.*, the M.C.C.P. at 20° in a stainless-steel tube of 8·75 mm. internal diameter and 1·75 mm. wall thickness was 4,900 atm., whilst in a glass tube of the same internal diameter and 1·25 mm. wall thickness the M.C.C.P. at the same temperature was below 3,800 atm.

The introduction of a number of pieces of glass into the steel tube caused no measurable alteration in the M.C.C.P., thus showing that the glass was not exerting a catalytic effect upon the reaction.

(c) *The presence of oxygen.* The presence of 0·5% by weight of benzoyl peroxide in solution in the monomer was found to have no effect upon the carbonisation pressure.



Curves showing variation of carbonisation pressure of cyclo*pentadiene with tube diameter.*

(d) *Diluents.* The effect of dilution was examined in Apparatus I, the same steel tube and a constant temperature of 40·0° (± 0·1°) being used for all experiments. Purified *n*-heptane was chosen as a non-polar solvent, and acetic acid and ethyl acetate as polar ones. The results are given in Table II.

TABLE II.

Variation of M.C.C.P. at 40° in the presence of diluents.

Diluent.	10%.	5%.	2%.	1%.	None.
n-Heptane	4000	3400	3200	3200	3100
Ethyl acetate	3800	3400			
Acetic acid	4200				

Products.—(a) *Gas.* A sample of the gas evolved during carbonisation was collected by attaching a valve to the top of the high-pressure chamber of Apparatus II. Analysis gave: CH_4, 92; H_2, 8%.

(b) *Carbonaceous material.* A sample of the carbonaceous residue was submitted to Prof. H. L. Riley, of King's College, Newcastle, and we are indebted to him for the following analytical and *X*-ray results. The carbon was first shaken for a long period with zinc and hydrochloric acid to remove mercury with which it had become impregnated during the violent reaction accompanying carbonisation. It was then further extracted with hydrochloric and hydrofluoric acids before analysis (Found: Ash, 2; C, 92·0; H, 2·6%).

X-Ray analysis of the purified material gave the measurements mc = 30·2 A. and ma = 14·5 A., and the crystallites can therefore be considered as being cylinders of which the average height is 30·2 A. with an average diameter of 14·5 A. They are thus rod-like as compared with the disc-shaped crystallites present in graphite.

(c) *Enveloping solid.* This was transparent to translucent, brown, and of a horny consistency. It formed an envelope round the carbonaceous matter varying in thickness according to the conditions under which it was formed; the smaller-diameter tubes in general produced comparatively thick envelopes. It was insoluble in all the usual organic solvents, failing even to swell during prolonged boiling with benzene (24 hrs.). After being well cleaned from adhering "carbon," a sample was analysed [Found: C, 83·8; H, 8·44; O(?), 7·76%].

DISCUSSION.

The occurrence of explosive reactions in the liquid phase is comparatively rare and their characteristics are, therefore, of some theoretical interest. In the present example an inspection of Fig. 1 (Part V, *loc. cit.*) shows that the region Y in which higher polymerisation of *cyclo*pentadiene occurs is restricted, and on the high-pressure side is bounded by the carbonisation zone in which a rapid exothermic change takes place. The two areas are quite distinct, and we have been unable to control or arrest carbonisation once it has started.

It has been shown that the carbonisation reaction has a well-marked induction period and critical pressure limits, features which are common to certain types of gas reactions in which chain processes are involved (cf. the oxidation of the higher hydrocarbons; Kane, Chamberlain, and Townend, J., 1937, 436).

Chains may start and/or terminate on the walls of the containing vessel or in the body of the reacting medium. In the former case the rate of development of the reaction with time is found to depend upon the surface/volume ratio of the vessel and upon its diameter. That the carbonisation of *cyclo*pentadiene under pressure is a homogeneous reaction is shown by the fact that increase in the surface/volume ratio produces no measurable change in the M.C.C.P.; and the view that a chain mechanism is involved, in which the chains terminate on the walls, is supported by the dependence of the M.C.C.P. on diameter. For a chain reaction a relationship between the C.C.P. and the tube diameter of the form $Pd^n =$ constant should exist, and when values of log P (Table I) are plotted against d this is found to be the case, a single straight line being obtained for 30° and two intersecting straight lines for 20°. The equation to the straight line at 30° gives the relationship $Pd^{0 \cdot 54} =$ constant.

Furthermore, the critical carbonisation pressure should be related to the absolute temperature by an equation of the type $\log_{10}(P/T) = A/T + B$, where A and B are constants. The results for the M.C.C.P. at temperatures from 13° to 40° give a satisfactory linear relationship between $\log_{10}(P/T)$ and $1/T$, the values for A and B being 1,180 and $-$ 2·80 respectively. It must be borne in mind, however, that the above equation also holds for a purely thermal reaction, and by itself is not a criterion of a chain mechanism. Moreover, a branching-chain reaction leading to an explosion is always accompanied by heat evolution, and the distinction between such a reaction and a purely thermal explosion is merely formal.

The comparative experiments in which steel and glass reaction tubes were employed show that thermal effects probably do influence the course of the reaction.* The ratio of the heat conductivities of steel and glass is 1 : 0·034, and the greater conductivity of steel necessitates the application of a pressure higher by upwards of 1,000 atm. than that required by glass to effect carbonisation. That the homogeneous reaction is not catalysed by oxygen or peroxide is shown by the experiments in which 0·5% of benzoyl peroxide was added.

It will be seen from Table II that when diluents are added to a proportion of up to 10% there is a progressive increase in the M.C.C.P. with increasing dilution; *e.g.*, at 40° an addition of 10% of *n*-heptane raised the critical pressure from 3,100 to 4,000 atm. At 5% dilution ethyl acetate and *n*-heptane gave the same critical pressures, but with increasing dilution there was a divergence in favour of a lower M.C.C.P. for ethyl acetate. 10% Dilution with acetic acid, on the other hand, gave an increased M.C.C.P., the pressure for *n*-heptane lying mid-way between those for acetic acid and ethyl acetate. The acetic acid

---

* The polymerisation of methyl methacrylate becomes self-heating as the medium becomes viscous through polymerisation. The suppression of convection is in this case an important factor.

experiments were noteworthy for the much greater rate of volume decrease, as shown by diminution of pressure during the initial stages of the experiment, and products from reactions at just below the M.C.C.P. contained much greater proportions of dimeride than were obtained without acetic acid under otherwise equal conditions. Any catalysis of polymerisation by acetic acid would lead to a more rapid rate of decrease of monomer concentration, and this would have the same effect as increased dilution, *i.e.*, the M.C.C.P. would be raised.

All the facts being taken into consideration, it seems probable that reaction chains are initiated by the series of reactions occurring in the region *Y* (higher polymerisation), and that branching occurs on the attainment of a critical pressure sufficiently high to ensure an adequate life for the chains. This view is supported by a study of the heats of combustion (Wassermann, J., 1935, 828; Becker and Roth, *Ber.*, 1934, **67**, 627) of *cyclo*pentadiene, its dimer, trimer, and tetramer. The polymerisation reaction proceeds with the evolution of about 25 kg.-cals. per g.-mol. of polymer formed at each step.

An alternative explanation would be that carbonisation is due to a high rate of polymerisation of a different type induced by the higher pressures. Insufficient evidence is as yet available to support this hypothesis, but the envelope of horny material produced in these reactions, presumably owing to the cooling and inhibiting effect upon carbonisation exerted by the walls of the reaction tube, bears some resemblance to the polymers which Staudinger and Bruson obtained by the action of stannic chloride on *cyclo*pentadiene (*Annalen*, 1926, **447**, 110). Their stannic chloride polymers were very sensitive to aerial oxidation and had to be purified in the absence of air for analysis.

The deficiency of 7·76% found in the analysis of our material is probably due to oxygen, and indicates a sensitivity to oxidation far in excess of that possessed by trimer and higher polymers formed under the conditions defined by area *Y*, possibly owing to a different molecular structure. The analogous deficiency in the analysis of the carbonised material is also probably due to oxidation, since, when removed from the reaction tube, the residue is in a finely divided and active condition.

Prof. H. L. Riley's *X*-ray analysis shows that the carbonised mass cannot be classified as either graphitic or amorphous. Since the distance between two corresponding layer planes in carbon is 6·79 A., that between two adjacent ones is 3·4 A., and thus the crystallites on an average contain about 10 layer planes, the mean diameter of each being 14·5 A. Since the side of each hexagon is 1·42 A. long it follows that each hexagon layer plane contains about 30 hexagons per plane. The only structure with which these crystallites may be compared is that of a low-temperature coke prepared at 550—600°.

The gas evolved during the reaction is principally methane (92%) and, as *cyclo*pentadiene has no carbon atom attached to more than two hydrogens, some hydrogenation process must be taking place in which $CH\vdots$, or $CH_2\colon$ groups are undergoing reduction to methane. To confirm this point, 5% solutions of various organic liquids in *cyclo*pentadiene were in turn subjected to the reaction. Aniline and pyridine gave ammonia, carbon tetrachloride gave hydrogen chloride, and hydrogen sulphide was produced from thiophen. The breakdown of such stable substances as carbon tetrachloride and thiophen is an indication of the large amount of energy released during this carbonisation reaction.

The authors wish to thank Prof. H. L. Riley, of King's College, Newcastle, for the *X*-ray examination and analysis of the carbonised material. One of them (B. R.) is also indebted to the Gas Light and Coke Company, Limited, for a Fellowship, and to the West Riding of Yorkshire Education Authorities for a maintenance grant.

Department of Chemical Technology,
Imperial College, London, S.W. 7.

[*Received, June 22nd*, 1939.]