414. *Liquid-phase Reactions at High Pressures. Part VII.* The Polymerisation of* 1 : 2-*Dichloroethylene.*

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The peroxide-catalysed polymerisation of *trans*-1 : 2-dichloroethylene has been examined at pressures up to 8000 atmospheres. High pressures favour the formation of polymers higher than dimer, and increase the yield of insoluble solid polymer.

THE study of *trans*-1 : 2-dichloroethylene was initiated to confirm that no dimerisation or isomerisation occurs under pressure, which could interfere with compression measurements on the liquid (Newitt and Weale, *J.*, 1951, 3092). Samples kept at pressures up to 10,000 atmospheres were recovered, as expected, with unchanged boiling point and refractive index. Experiments have been extended to dichloroethylene containing benzoyl peroxide, as the effect of pressure on the catalysed polymerisation is of interest.

In contrast with 1 : 1-dichloroethylene, the symmetrical isomers do not polymerise readily. Mahncke and Noyes (*J. Amer. Chem. Soc.*, 1936, **58**, 932) report the formation of very small quantities of solid from the vapour of both isomers on irradiation by ultra-violet light. The product from the *cis*-form melted sharply at 103·5—104° (Found: Cl, 72·5. Calc. for $C_2H_2Cl_2$: Cl, 73·2%). Various patent specifications (G.P. 718,057; Bauer, B.P. 517,195, F.P. 840,867, U.S.P. 2,267,712) describe the liquid-phase polymerisation of both isomers, with peroxide catalysts or in ultra-violet light: the products are almost entirely liquid polymers, with total yields up to 35%, and a weight ratio dimer : higher polymers varying from 0·5 to 3·5 at higher temperatures. Bauer (F.P. 840,867), by prolonged refluxing (200 hours) of the *trans*-isomer with 1% by weight of benzoyl peroxide, obtained 16·6% of dimer, 13·5% of higher liquid polymers, and also 1·5% of white powder, insoluble in ether.

Breitenbach, Schindler, and Pflug (*Monatsh.*, 1950, **81**, 21) obtained 46·5% and 43·7% conversion of *trans*- and *cis*-isomers, respectively, at 90° (1 mol.% of benzoyl peroxide) into a dimer (cryoscopic measurements in benzene). At lower temperatures, with 0·1 mol.% of *o*-bromobenzoyl peroxide, the *trans*-isomer yielded an insoluble white polymer (2·7% after 100 hours at 40°) and up to 10% of liquid polymers. These authors attribute the first observation of an insoluble polymer of *trans*-dichloroethylene to Ebert and Büll (Büll, Diss., Würzburg, 1931), who initiated the reaction photochemically. Later, Ebert and Eichinger (Eichinger, Diss., Vienna, 1944) could not obtain a similar product from the *cis*-isomer.

Frank and Blackham's results (*J. Amer. Chem. Soc.*, 1950, **72**, 3283) are quoted in part in the table below. In addition, at 70° (72 hours), they obtained the high yield of 71·0% of polymers, with a dimer : higher polymer ratio of 1 : 1, but they do not describe a solid polymer. The results of an experiment at atmospheric pressure with a *cis–trans* mixture are included in the table. No detectable amount of solid polymer was found, and the total yield is slightly less than was reported by Frank and Blackham; the dimer : higher polymer ratio is between their limits for the pure isomers.

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* Part VI, *J.*, 1939, 1770.

The table illustrates the effect of high pressures on the catalysed polymerisation of *trans*-dichloroethylene. The total yields increase markedly with temperature and to a small extent with pressure. High pressures tend to decrease and higher temperatures to increase the ratio of dimer to higher polymers, and this ratio is always lower than at ordinary pressure. The ratio was not determined at 15° (5% yield), or in the experiments at 8000 atm. where, instead of the usual mixture of monomer, liquid polymers, and gelatinised white solid, the product was a soft waxy plug, difficult to separate into its components. At 85—100°, depending on pressure, decomposition led to a carbonised product containing chlorinated methanes.

Polymerisation of 1 : 2-*dichloroethylene* (*with* 1 *mol.% of benzoyl peroxide*).

Reaction time (hrs.)	Temp.	Pressure (atm.)	Yield, %	Dimer, %	Higher liquids, %	Solid, %	Wt. ratio, dimer : higher polymers
96	61—78·4° (*cis*)	1	57·2	39·3	17·9	—	2·2
96	49—64·4	1	53·5	19·2	34·3	—	0·56
140	55—65 (*cis–trans*)	1	51	30	21	—	1·5
70	15	3000	5	(5)		—	—
70	35	3000	17	3	11	3	0·21
70	75	3000	75	22·5	42·5	10	0·43
35	75	3000	72	22	43	7	0·44
140	75	3000	82	22	50	10	0·37
70	75	5000	77	10	55	12	0·15
70	75	8000	90	(70)		20	—

The tabulated results are for *trans*-dichloroethylene, except where indicated. The first two are quoted from Frank and Blackham (*loc. cit.*) who used 1·2 mol.% of peroxide.

High pressures are well known to exert a profound effect on polymerisation reactions (Part II, *J.*, 1937, 1784). Merrett and Norrish (*Proc. Roy. Soc.*, 1951, *A*, 206, 309) attribute the acceleration of styrene polymerisation to a speeding up of the "slow" bimolecular propagation reaction, which probably occurs in the present case. Here the propagation competes with the formation of dimer by transfer from the active dimer radical to the monomer. This may be formulated (cf. Mayo, Wilzbach, and van Meter, *J. Amer. Chem. Soc.*, 1948, **70**, 4069), so that a chlorine atom passes from a dimer radical to a molecule of monomer, or *vice versa*, but in either case it must be less (if at all) accelerated by pressure than is the propagation reaction.

EXPERIMENTAL

trans-Dichloroethylene, b. p. 48·5—49°, $n_{\mathrm{D}}^{19\cdot5}$ 1·4465 was obtained by fractionation of technical material. A small amount of *cis*-dichloroethylene, (b. p. 60—61°, $n_{\mathrm{D}}^{19\cdot5}$ 1·4482) was made by bromine-catalysed isomerisation (Jones and Taylor, *J. Amer. Chem. Soc.*, 1940 **62**, 3480). The reacting liquid was confined over mercury in Pyrex-glass tubes, which were immersed in oil in steel pressure-vessels. The reaction product was taken up in ether, solid polymer being recovered by filtration and washing with ether. The ether and unchanged monomer were removed by evaporation, and the dimer was separated from higher liquid polymers by distillation at reduced pressure.

The dimer, b. p. 95—100°/30 mm., n_{D}^{20} 1·517 (in agreement with previous observations), identified by Bauer as 1 : 3 : 4 : 4-tetrachlorobut-1-ene, did not react in the presence of benzoyl peroxide at the highest pressure used. The dry solid polymer is a white amorphous powder (Found: Cl, 74·6. Calc. for $[CHCl]_n$: Cl, 73·2%), which swells and becomes gelatinous in contact with organic solvents but does not dissolve. It is unchanged at 160—170°, softens slightly at higher temperatures, and fumes at 215°. The solid is obviously not identical with Mahncke and Noyes's sharp-melting product, but is probably the same as that obtained by Bauer and by Breitenbach *et al.* The same substance was obtained (8% yield) from the *cis*-isomer at 75°/3000 atm.

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