

Liquid-phase Reactions at High Pressure. Part IX. The Polymerisation of Some 1 : 2-Disubstituted Ethylenes.*

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The peroxide-catalysed polymerisation of twelve 1 : 2-disubstituted ethylenes at hydrostatic pressures up to 10,000 atm. has been examined. Five of these substances, which do not polymerise readily or at all at ordinary pressures, give high yields of polymer under the conditions employed.

The modes by which pressure may accelerate the polymerisation are discussed. In two cases failure to react, or to proceed beyond the dimer, is attributed to steric hindrance, and in the case of *tert.*-butyl cinnamate it is probable that steric hindrance occurs but is reduced at high pressures. The relation of polymerisability to the index of free valence is considered in a number of cases.

HIGH pressures are known to accelerate the polymerisation of olefins, and to favour higher polymers. The effect has been extensively studied, but little attention has been paid to 1 : 2-disubstituted ethylenes, which are much less readily polymerisable at ordinary pressures than are olefins which contain the =CH₂ grouping. The peroxide-catalysed polymerisation of twelve substances of this class has now been investigated at pressures up to 10,000 atm., and the results are correlated with the structure of the monomer.

Compounds of this kind previously investigated include 1 : 2-dichloroethylene (Weale, *J.*, 1952, 2223), crotonaldehyde (Klaasens and Gisholf, *J. Polymer Sci.*, 1953, 10, 149), diethyl fumarate (Starkweather, *J. Amer. Chem. Soc.*, 1934, 56, 1870), indene (Bridgman and Conant, *Proc. Nat. Acad. Sci.*, 1929, 15, 680; U.S.P. 1,953,116; Fr.P. 699,555; Tammann and Pape, *Z. anorg. Chem.*, 1931, 200, 113; Klaasens and Gisholf, *loc. cit.*), ethyl cinnamate (Sapiro, Linstead, and Newitt, *J.*, 1937, 1784), and cyclohexene (Zelinskii and Vereshchagin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1954, 44; Nemtzov, Nizokina, and Soskina, *J. Gen. Chem. U.S.S.R.*, 1938, 8, 1303).

The last four compounds have been further studied, and they are listed with the other monomers used in the following section, which briefly summarises the extent to which the compounds undergo thermal and peroxide-catalysed polymerisation at ordinary pressures. Some results are included for ionic polymerisation at 1 atm.

At normal pressure, the thermal polymerisation of cyclohexene yields dimers and trimers, and small quantities of higher polymers (Nemtzov *et al.*, *loc. cit.*; Lecomte, Leendertse, and Waterman, *Compt. rend.*, 1947, 224, 193) and with benzoyl peroxide low

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polymers containing benzoxyloxy-groups are formed (Kaishi Noma and Takashi Tsuchida, *Chem. High Polymers, Japan*, 1948, 5, 166). For stilbene, quantitative data are lacking, but it has been shown to form small amounts of low polymer (*e.g.*, Schildknecht, "Vinyl and Related Polymers," John Wiley & Sons, Inc., New York, 1952, p. 156). Indene has been more widely studied. Thermal polymerisation in the range 120—175° is a first-order reaction, producing polymers of a wide range of molecular weights (Bergmann and Taubadel, *Ber.*, 1932, 65, 463; Dostal and Raff, *Z. phys. Chem.*, 1936, 32, B, 417; Breitenbach, *Z. Elektrochem.*, 1937, 43, 323; Corrin, *J. Polymer Sci.*, 1947, 2, 257; Schmid and Gutman, *ibid.*, 1948, 3, 325). Analysis of a sample of polyindene gave molecular weights in the range 200—1200 (Pass, *ibid.*, p. 327).

Using SbCl_5 and SnCl_4 as catalysts, Whitby and Katz (*J. Amer. Chem. Soc.*, 1928, 50, 1160) obtained polymers corresponding to the formula $(\text{C}_9\text{H}_8)_{29}$ and found that the molecular weight decreased with higher reaction temperatures. They also report a relation between the melting point of the polymer fraction and its molecular weight. Marvel and McCain (*ibid.*, 1953, 75, 3272) produced up to 10% of polymerisation by heating ethyl cinnamate with benzoyl peroxide or $\alpha\alpha'$ -azobisisobutyronitrile at 60° for one month. Methyl cinnamate under similar conditions for 13 days yielded 2% of polymer. The molecular weights were 7600 and 2300, respectively.

Diethyl and dimethyl maleate, treated in turn with large quantities of benzoyl peroxide ($\frac{1}{2}$ — $\frac{1}{3}$ mol.), at 53° for 700 hr. yielded polymers with an average chain length of four monomer units (Marvel *et al.*, *ibid.*, 1947, 69, 52). Diethyl fumarate in the presence of $\alpha\alpha'$ -azoisobutyronitrile gave some polymer (Walling and McElhill, *ibid.*, 1951, 73, 2819).

Crawford has studied the polymerisation of methyl α -*tert.*-butylacrylate (Crawford and Smith, *J.*, 1952, 1220; Crawford, *J.*, 1953, 2658). Small amounts of low polymer were formed on exposure to ultraviolet light or on reaction with benzoyl peroxide. The yield of dimer was increased by the action of sodium in liquid ammonia.

There are no data for the polymerisation of maleic anhydride, except as a copolymer; and 1 : 2-dibromoethylene, *n*-butyl cinnamate, and *tert.*-butyl cinnamate have apparently not been polymerised.

EXPERIMENTAL

Apparatus.—The high-pressure apparatus used was essentially that described in previous papers in this series (Newitt, Linstead, Sapiro, and Boorman, *J.*, 1937, 876; Raistrick, Sapiro, and Newitt, *J.*, 1939, 1761), a steel container replacing the glass reaction tube at pressures above 5000 atm.

Materials and Procedure.—The conditions of reaction and molecular weights are recorded in Table 2.

Benzoyl peroxide (B.D.H.) for use as catalyst was purified by Augood, Hey, and Williams's method (*J.*, 1952, 2100) and kept in a vacuum-desiccator. Unless specified differently, it was added in the proportion of 1 mole % of monomer.

*cyclo*Hexene (B.D.H.) was stored over calcium chloride and freshly distilled before use; it had b. p. 83.4°, n_D^{18} 1.4472. After reaction, the product was washed with water, to remove catalyst residues, dried (CaCl_2), and distilled under reduced pressure. The residue consisted of a yellow oil representing about 1% of the monomer used.

trans-Stilbene (B.D.H.), recrystallised three times from absolute alcohol, and dried under vacuum, had m. p. 125°. Stilbene (2 g.) was dissolved in pure toluene (25 ml.) together with the catalyst, and reaction allowed to proceed under pressure. After evaporation of the toluene at room temperature (heating tended to cause some decomposition), the residue consisted of crystals of stilbene with traces of a viscous oil, n_D^{21} 1.4860 (n_D^{20} for *cis*- and *trans*-stilbene, 1.61 and 1.63—1.68, respectively).

Indene (B.D.H.), fractionated through a glass-packed column, had b. p. 183°, n_D^{25} 1.5650. After reaction, in every case, the solution had darkened slightly. The percentage polymerisation was estimated from the change in refractive index, Breitenbach and Bremer's data (*loc. cit.*) being used; $n_D^{15.5}$ 1.5700 for indene + 1% of catalyst; 1.5805 and 1.6020 for the 5100- and 10,000-atm. fractions respectively.

Polyindene was isolated as a white powder by precipitation with methanol from a solution of the reaction products in ether. This powder, consisting of polymers of very different

molecular weights, was further separated by fractional precipitation with ethanol from a solution in benzene. The physical properties of the resulting polyindene fractions are shown in Table 1.

TABLE 1. *Physical properties of polyindene fractions.*

Fraction	Melting range	Viscosity (sec.) *	M
5100 atm., No. 1	230—235°	155	820 †
2	215—225	154	710
3	205—210	151	450
4	(Liquid)	—	Dimers and trimers
10,100 atm., No. 1	210—220	155	820
2	205—210	153	620
3	(Liquid)	—	Tetramers and below

* Time of flow in sec. for a 1% solution in benzene, pure benzene requiring 145 sec.

† 797 cryoscopically in benzene.

The values of the molecular weights were obtained by extrapolation on a melting point-molecular weight curve drawn from the results of Whitby and Katz (*loc. cit.*).

Maleic anhydride (B.D.H.), purified by distillation, and recrystallised from chloroform had b. p. 196°; 4 g. of maleic anhydride + 1 mole % of benzoyl peroxide were dissolved in 25 ml. of pure toluene and allowed to react under pressure. The product, an insoluble, sticky, yellowish solid, was dissolved in acetone, and the solvent evaporated under reduced pressure. The residue was a hard brown solid which charred when heated. Several experiments under the same conditions did not give good agreement, the yield varying from 50 to 70%. The highest value of the molecular weight (determined cryoscopically in water, since the product was insoluble in benzene) was 154.

Diethyl maleate (B.D.H.) was distilled under reduced pressure, and the fraction of b. p. 108°/17mm., n_D^{19} 1.4398, was used. The reaction products were washed with water and dried (CaCl₂). After distillation under reduced pressure, the residue, an oil which tended to char when heated, represented about 10% yield.

Diethyl fumarate (B.D.H.), purified in the same way as the maleate, had b. p. 98°/14 mm., $n_D^{18.5}$ 1.4411. At 2000 atm. the product was a viscous oil, which was dissolved in ether, washed with water, and dried. Evaporation under reduced pressure left two fractions, the first (n_D^{20} 1.4595) readily soluble in ether, and the other (n_D^{20} 1.4790) soluble in benzene.

At higher pressures, the product was a transparent solid which softened at 100° and finally melted at about 360°. The polymer was soluble in benzene, acetone, ethanol, and pyridine.

1 : 2-Dibromoethylene (B.D.H.), dried (CaCl₂) and freshly distilled before use, had b. p. 110°, n_D^{20} 1.5418. After reaction, the liquid product was brown. It was dissolved in ether, washed with water, and dried. On distillation under reduced pressure, there remained a few drops of an oil, amounting to 2—3% yield.

Methyl cinnamate (B.D.H.), fractionated under reduced pressure, had b. p. 127°/13.5 mm. Because it was suspected that the monomer (m. p. 33°/1 atm.) solidified under pressure, the reaction was carried out in ethanol. The product was a white powder which was filtered off, washed with alcohol, and dried *in vacuo*. The polymer was fairly soluble in benzene and in boiling pyridine. It represented 9% polymerisation. It remained unchanged up to 360°, and was not heated further.

Ethyl cinnamate (B.D.H.), dried (CaCl₂) and distilled under reduced pressure, had b. p. 140°/14 mm., n_D^{19} 1.5590. After reaction, the contents of the reaction vessel had become a tough opalescent solid. The polymer was soluble in benzene and boiling chloroform, and to some extent in boiling ethanol. It softened at about 100° and tended to crumble as the temperature was raised to 290°. At 340°, it became brittle.

n-Butyl cinnamate, prepared from cinnamic acid (Jeffery and Vogel, *J.*, 1948, 658), was distilled under reduced pressure; it had b. p. 159°/15 mm., n_D^{20} 1.5400. After reaction under pressure, the product was a transparent solid, which was soluble in benzene, and to a smaller extent in ethanol. Its behaviour, when heated, was similar to that of ethyl cinnamate.

tert.-Butyl cinnamate, prepared from the acid chloride and *tert.*-butyl alcohol (Abramovitch, Shivers, Hudson, and Hauser, *J. Amer. Chem. Soc.*, 1943, 65, 986; *Org. Synth.*, 1944, 24, 19), a yellow oil, was distilled under reduced pressure; it had b. p. 160°/14 mm., n_D^{19} 1.5414 (Found : C, 76.15; H, 8.0. Calc. for C₁₃H₁₆O₂: C, 76.4; H, 7.9%). After reaction under pressure, the product was a transparent yellow solid similar in appearance to, but rather softer than,

poly-(*n*-butyl cinnamate). Some traces of unchanged monomer could be discerned between the polymer surface and the Pyrex tube. Heating produced the same reaction as with the ethyl and the *n*-butyl polyester.

Methyl α -*tert*-butylacrylate (I.C.I. specially purified, n_D^{20} 1.4272), without further treatment, was treated under pressure with 6.2 mols. % of benzoyl peroxide. The products, which were liquid, were taken up with ether and distilled at 11 mm. The monomer distilled over at 28°, leaving a stiff translucent jelly, which remained unaltered for 1 hr. at 100°/11 mm. (n_D^{20} 1.4840). The amount, corrected for catalyst residues, represented 19% of polymerisation. A further sample of monomer was treated with 6.2 mols. % of benzoyl peroxide with the further addition of 0.5 mol. % of *tert*-butyl perbenzoate as extra catalyst. After similar treatment to the previous sample, a clear transparent viscous liquid remained (n_D^{20} 1.4720), corresponding to 66% of the original sample.

Determination of Molecular Weights.—The molecular weights of polymers were measured in three ways (cf. col. 9 of Table 2).

Cryoscopic method (C). The so-called "Beckmann method" was used, the apparatus being the same as that described by Skau and Wakeman (Weissberger, "Physical Methods of Organic Chemistry," Interscience Publ., 1949, Vol. 1, p. 93). B.D.H. "Molecular-weight" benzene was the solvent. Before use, it was further dried by storage over calcium chloride for several weeks, during which the m. p. gradually rose, and finally attained a constant value. This was then taken as the correct m. p.

TABLE 2. Reaction conditions and polymerisation products.

1. Substance	Reaction conditions.				Reaction products.			
	2. Catalyst*	3. Temp.	4. Press. (atm.)	5. Time (hr.)	6. Yield (%)	7. <i>M</i>	8. Order	9. Method
<i>cyclo</i> Hexene	—	60°	3300	22	<1	—	—	—
"	—	90	3400	22	<1	—	—	—
"	*	60	3700	21	1	—	—	—
"	*	90	3700	21	1	—	—	—
Stilbene (S)	*	90	5000	24	—	—	—	—
Indene (1)	—	20	9000	24	some	—	—	—
" (2)	—	20	12,000	72	10	—	—	—
"	*	90	5100	23	17	850	7	(C & V)
"	*	90	10,100	23	50	850	7	(C & V)
Maleic anhydride (S)	*	60	4900	23	15—20	150	1—2	(C)
" (S)	*	90	4900	24	50—70	154	1—2	(C)
Diethyl maleate	—	90	4200	18	2	—	—	—
"	*	60	1800	23	6	—	—	—
"	*	60	1800	22	10	—	—	—
Diethyl fumarate ...	*	60	2000	22	60	381—738	2—4	(C)
" (3)	*	59	2000	22.5	92.5	—	—	—
"	*	60	5000	23	98	1000	6	(C)
"	*	57	10,000	24	~100	1530	9	(C & V)
Methyl cinnamate (S)	*	60	5000	23	9	4000	24	(O)
Ethyl cinnamate (4)	—	125	4000	240	58.5	—	—	—
"	*	100	5000	23	99	4900	27	(O)
<i>n</i> -Butyl cinnamate... ..	*	90	4400	22	98	6100	29	(O)
<i>tert</i> -Butyl cinnamate	*	90	4400	22	90	3800	18	(O)
1 : 2-Dibromoethylene	*	80	5300	23	1	—	—	—
"	*	90	5100	47	2—3	—	—	—
"	*	100	10,000	23	3	—	—	—
Methyl α - <i>tert</i> -butyl acrylate	†	100	10,000	23	19	230	1—2	(C)
"	† + (5)	130	10,000	23	66	320	2—3	(C)

* The asterisk in col. 2 denotes 1 mol. % of benzoyl peroxide; † denotes 6.2 mols. % of benzoyl peroxide. (S) Indicates that the reaction was carried out in a solvent. (1) and (2) Results reported by Bridgman. (3) Results reported by Starkweather. (4) Results reported by Newitt *et al.* (5) Additional catalyst was 0.5% of *tert*-butyl perbenzoate.

Viscosity method (V). The instrument used throughout was an Ostwald No. 1 capillary viscometer. While readings were taken the instrument was immersed in a thermostat at 20°. The time of flow was the mean of at least three runs. In calculating the molecular weights from the viscosity data the simple Staudinger relation $[\eta] = KM$ was used in view of the comparatively low order of molecular weights.

Osmotic pressure method (O). These measurements were carried out in the Chemical Research Laboratory, Teddington. A polyvinyl alcohol semipermeable membrane was found to be the most suitable. Details of the process are similar to those reported by Hookway and Townsend (*J.*, 1952, 3190).

DISCUSSION

As Table 2 shows, although some of the compounds do not react to any significant extent or give products of very low molecular weight, the polymerisation of the others is favoured by high pressure. Higher yields of polymer are obtained in much shorter times than those recorded at normal pressures, as is well shown by, *e.g.*, methyl and ethyl cinnamate. There is also an increased degree of polymerisation. The polymer from diethyl fumarate at 5000 atm. contains six units, and at 10,000 atm. nine units. Polyindene, however, contains seven units whether it is formed at 5100 or 10,000 atm. These broad findings accord with previously reported effects of pressure on the polymerisation of other types of substituted ethylenes.

More than one mechanism may be operative in each stage of a radical-chain polymerisation. Thus chain termination may take place by mutual combination of two radicals, disproportionation between two radicals, chain transfer to monomer, or chain transfer to polymer. Where a solvent is used, there may also be interaction between radicals and solvent molecules. The observed effects of pressure may, therefore, be explained in a number of different ways, involving retardation or acceleration of the various stages. Merrett and Norrish (*Proc. Roy. Soc.*, 1951, *A*, 206, 309), in the only detailed study of an individual polymerisation at high pressure so far published, found that the chain propagation was accelerated about 10-fold at 60°/5000 atm., while the initiation reaction rate was hardly affected.

It is probable that acceleration of the propagation stage occurs in those of the nine reactions responsive to pressure which yield polymers. Acceleration of organic reactions by pressure is generally found when the formation of the transition state is accompanied by a local decrease in volume. There is also evidence that pressure may overcome some degree of steric hindrance when this is not sufficient to prevent the reaction completely at ordinary pressure (Weale, *J.*, 1954, 2959). An acceleration of propagation relative to termination by the chain-transfer mechanism is qualitatively understandable, as the bimolecular addition of growing polymer to monomer will proceed through a more compact transition state than a reaction in which bond-lengthening is involved.

The monomers studied may be grouped into the three categories: (*a*) symmetrical olefins, *viz.*, stilbene, 1:2-dibromoethylene, maleic anhydride, diethyl maleate, and diethyl fumarate; (*b*) asymmetrical olefins, which include the cinnamic esters and methyl α -*tert.*-butylacrylate; (*c*) the homocyclic olefins *cyclohexene* and *indene*.

(*a*) The symmetrical olefins include two of the three most resistant to polymerisation. 1:2-Dibromoethylene hardly reacts at all even at 10,000 atm., although 1:2-dichloroethylene polymerises quite readily at this pressure (*idem*, *J.*, 1952, 2223). This result illustrates the inability of hydrostatic pressure to overcome a high degree of steric hindrance. A model of the chloro-substituted polymer was strain-free, but, owing to the greater size of the bromine atoms, a model of the bromo-polymer could not be made without a large amount of strain.

The two esters and maleic anhydride all reacted; the failure to obtain a product of high molecular weight from the latter may be due to the use of a solvent for this reaction. In these instances, steric hindrance probably does not influence the reaction rates. The greater reactivity of the fumarate than of the maleate has been observed in copolymerisations at ordinary pressure (Lewis, Walling, Cummings, Briggs, and Mayo, *J. Amer. Chem. Soc.*, 1948, 70, 1519; Doak, *ibid.*, p. 1525; Mayo, Lewis, and Walling, *ibid.*, p. 1529; Lewis and Mayo, *ibid.*, p. 1533; Walling, Seymour, and Wolfstirn, *ibid.*, p. 1544). Lewis and Mayo attribute this to the fact that the fumarate but not the maleate may assume a configuration in which the carbonyl and olefin groups are coplanar, so facilitating resonance-stabilisation of the free radical. As would be expected, this difference persists at high pressures.

The lack of reactivity of stilbene is also not due to steric hindrance, and the ethylenic carbon atoms resemble in inertness those of *cyclohexene*, which is discussed below.

(b) Among the asymmetrical olefins, the four esters of cinnamic acid were all polymerisable much more readily than Marvel and McCain (*loc. cit.*) found at ordinary pressure. The rather low yield from methyl cinnamate is probably due to interference by solvent in the initiation stage, as the order of polymerisation compares with that of the ethyl ester. In these compounds, the resonance stabilisation of the radicals (conjugation of the benzene nucleus with the double bond) is unlikely to be affected by the ester group, and the contribution of the latter should depend almost entirely on its steric effect. The order of the polymers is very similar as far as *n*-butyl, which is probably sufficiently flexible for there to be no hindrance to propagation. The polymer from *tert*-butyl cinnamate is, however, of definitely lower order, and models indicate a considerable degree of steric strain in this reaction. In view of the excellent yield of polymer, this may well be an example of high hydrostatic pressure overcoming steric hindrance.

The yield from methyl α -*tert*-butylacrylate is also increased at 10,000 atm. over that obtained by Crawford (*loc. cit.*) at 1 atm. The order of the polymer, however, remains low, and the steric hindrance which Crawford found to oppose head-to-tail propagation (but not head-to-head dimerisation) is presumably too great to be much affected by compression of the reacting system.

(c) Of the two homocyclic olefins examined, indene was found to polymerise as previously reported, but the yield from *cyclohexene* was very low. These reactions are unhindered, and the low reactivity of *cyclohexene* (which tends to disappear at high temperature and pressures, according to Vereshchagin *et al.*, *loc. cit.*) cannot be ascribed to this cause.

Relation of Polymerisability to the Index of Free Valence.—In radical polymerisation the free radical in attacking the monomer seeks an unpaired electron. Thus the energy required to localise one unpaired electron at a particular carbon atom of the monomer is a measure of the compound's readiness to under go a free-radical chain-reaction (Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900; Coulson, *Research*, 1951, **4**, 307). On a particular atom the concentration of electrons not engaged in bonding, and therefore available for reaction, is known as the index of free valence. This quantity has been calculated in a number of cases, and some success has been achieved in establishing a relationship between the free valence and the reactivity towards free radicals (Roitt and Waters, *J.*, 1952, 2695; Kooyman and Farenhorst, *Nature*, 1952, **169**, 153; Kerichi Fukui, Teijiro Yonezawa, Chikayoshi Nagata, and Haruo Shangu, *J. Chem. Phys.*, 1954, **22**, 1433). Therefore information about radical polymerisation might be obtained by studying the free valences of the carbon atoms at both ends of the double bond in the compounds mentioned above.

TABLE 3.

1.	2.	3.	4.	5.	6.	7.
Substance	C atoms	Free valence	Ref.*	Free valence	Frontier electron density	Bound valence
Benzene	all	0.40 0.347	<i>a</i> <i>b</i>	0.40	—	2.000
<i>cyclo</i> Hexene	1 & 2	—	—	0.952	—	—
Naphthalene	α	0.489 0.40	<i>c</i> <i>b</i>	0.427	0.362	1.875
	β	0.452	<i>c</i>	0.390	0.138	2.015
Indene	1	0.372	<i>d</i>	0.424	—	—
	2	0.616	<i>d</i>	0.668	—	—
Stilbene	α	0.481	<i>c</i>	0.497	0.340	1.882
Styrene	α	0.415	<i>c</i>	0.547	0.259	1.927
	β	0.821	<i>c</i>	0.907	0.683	1.619

* *a*, Coulson, "Valence," Oxford, 1952, p. 254. *b*, Kooyman and Farenhorst, *Nature*, 1952, **169**, 153. *c*, Vroelant, *Compt. rend.*, 1952, **235**, 958. *d*, Pullman and Berthier, *Bull. Soc. chim. France*, 1948, 551.

In Table 3 the values of the index of free valence taken from a number of sources are recorded in col. 3. These values were calculated by using bond-length data from the

following sources: stilbene (Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568), styrene (Penney and Kynch, *ibid.*, 1938, *A*, **164**, 409), naphthalene (Abrahams, Robertson, and White, *Acta Cryst.*, 1939, **2**, 233), indene (Pullman and Bertier, *Bull. Soc. chim. France*, 1948, 551), and benzene (Coulson, *op. cit.*, pp. 253, 254). See col. 5.

Frontier electron densities, quantities calculated by Kerichi Fukui *et al.* (*loc. cit.*), which are similar to the free valence, are shown in col. 6.

The "bound valence," which is complementary to the free valence (Ruedenberg and Sherr, *J. Chem. Phys.*, 1953, **21**, 1565; Sherr, *ibid.*, p. 1582), is included in col. 7.

In the case of *cyclohexene* there are no reliable data for the bond lengths. Some workers have assumed the values 1.35 Å and 1.54 Å for the C=C and the C-C bond, respectively (Beckett, Freeman, and Pitzer, *J. Amer. Chem. Soc.*, 1948, **70**, 4227; Lister, *ibid.*, 1941, **63**, 143). These figures lead to the high value of 0.932 for the free valence. It seems, however, unlikely that the double bond and the two adjacent single bonds do not undergo some sharing of order. Indeed, the values of the ionisation potential for benzene (9.52 and 9.45 eV) and *cyclohexene* (9.24 eV) (Morrison and Nicholson, *J. Chem. Phys.*, 1952, **20**, 1021) suggest that the double-bond order is not very different from that of benzene, with the remaining bonds becoming progressively more single in character. As for the other values in the Table, it is clear that, although there are differences due to the method of calculation, the general agreement is very good.

From these results it is seen that both styrene and indene, which polymerise readily, have a high free valence at one end of the double bond. A free radical can attach itself at that point, and the resulting complex is another free radical with a high free valence at the second carbon atom.

In the case of stilbene the free valence is small on both the carbon atoms, and such a reaction cannot easily take place. Benzene, however, has also a small free valence, but is subject to attack by benzoyl peroxide (Gelissen and Hermans, *Ber.*, 1925, **58**, 285). It is probable that the symmetry of the ring allows the excess of electron density to be shared among the remaining carbon atom sites.

cyclohexene is not easily explained. However, the considerable strain in the ring structure will probably go towards neutralising the effect of the apparent high free valence. This is supported by the fact that at high temperatures, *i.e.*, with sufficient energy input, the molecule will readily undergo catalysed polymerisation (Zelinskii and Vereshchagin, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1945, **44**; Nemtsov, Nizokina, and Soskina, *J. Gen. Chem. U.S.S.R.*, 1938, **8**, 1303).

Because reliable data are only available for a few compounds, the evidence is not complete. However, it seems reasonable that polymerisability of these hydrocarbons when steric hindrance is absent may be related to the size of the free valence on the carbon atoms of the "active" double bond.

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