580. *The Reaction of Sulphur and Sulphur Compounds with Olefinic Substances. Part X.[1] The Kinetics of the Reaction of Sulphur with* cyclo*Hexene and Other Olefins.*

By G. W. Ross.

The interaction of sulphur and *cyclo*hexene at 110—140° has been studied dilatometrically. The reaction is autocatalytic, and in the early stages the rate is proportional to the square root of the sulphur, olefin, and product concentrations. Other mono-olefins react similarly. 2 : 6-Dimethylocta-2 : 6-diene reacts more slowly than comparable mono-olefins, despite having two double bonds per molecule, and this feature is associated with the formation of cyclic monosulphides in addition to the cross-linked poly-sulphides similar to those formed from mono-olefins.

The kinetic and product data are consistent with a polar, not a free-radical, chain reaction.

As stated in Part VIII,[2] the kinetic studies now reported are complementary to product studies described in Parts VIII and IX in a programme of work aimed at elucidating the mechanism of sulphur–olefin interaction at about 140°.

Attention has been given mainly to the reaction of sulphur with *cyclo*hexene, because the latter is a relatively good solvent for sulphur, but reactions with 1-methyl*cyclo*hexene, oct-1-ene, hept-2-ene, 2-methylpent-2-ene, 2 : 6-dimethyloct-2-ene, and the 1 : 5-diene, 2 : 6-dimethylocta-2 : 6-diene, have also been examined. The rate of reaction increases until about 20% of the sulphur has reacted and then continues at an almost steady value until nearly all the sulphur is consumed. Further reaction between the product and excess of olefin proceeds at a diminishing rate. Kinetic analysis has been confined mainly to the period of accelerating rate (r_a), and the information obtained appears to justify this procedure rather than considering the steady maximum rate (r_m).

EXPERIMENTAL

Materials.—*cyclo*Hexene was freed from peroxides and purified as described by Bateman and Hughes[3] and stored under nitrogen at $-25°$ until required. The other olefins were as

[1] Part IX, Bateman, Glazebrook, and Moore, preceding paper.
[2] Bateman, Glazebrook, Moore, Porter, Ross, and Saville, *J.*, 1958, 2838.
[3] Bateman and Hughes, *J.*, 1952, 4594.

described in Parts VIII [2] and IX.[1] Immediately before use, the olefin was passed under nitrogen through activated alumina and then distilled under a high vacuum. Sulphur was purified by Bacon and Fanelli's method,[4] and converted into a form suitable for introduction into the dilatometer (capillary tube of 1·5 mm. internal diameter) by grinding and sieving or by recrystallisation from *cyclo*hexane. *cyclo*Hexane was purified by nitration and fractionation (b. p. 80·5°/756 mm.), followed by passage through a column of silica gel. Pure 2 : 2-diphenyl-1-picrylhydrazyl and dibenzyl tetrasulphide were supplied by Lyons and Watson,[5] and Moore, respectively. 1-Azobis-1-phenylpropane was prepared as described by Cohen, Crosvos, and Sparrow.[6] Benzoquinone, trichloroacetic acid, triethylamine, and ethyl sulphide were purified by standard methods; other substances were of " AnalaR " grade and were used directly.

Procedure.—Reaction was followed by observing the volume contraction in a dilatometer with a cathetometer. The dilatometer had a bulb of capacity 4—8 ml. and a capillary tube of 1·5 mm. internal diameter. The olefin was degassed and then distilled at $<10^{-3}$ mm. into the dilatometer containing a weighed quantity of sulphur. Rapid dissolution of the sulphur was effected with vigorous magnetic stirring. Temperature variation during reaction was generally $<0·01°$; if greater (as over long periods) the volume changes were corrected. Allowance was made for the initial time lag (*ca.* 3 min.) in reaching temperature equilibrium in the thermostat. At the end of a run, the dilatometer was cooled rapidly, the products were transferred to a wide-mouthed tube and degassed, and the unchanged olefin was distilled into a receiver cooled in liquid air and weighed. Unchanged sulphur in the residue was separated by successive filtration and cooling to $-25°$; the quoted sulphur contents of the polysulphides are probably a little high owing to the solubility of sulphur in these products. Weighings were made at each stage in these operations when it was necessary to correlate volume changes with extent of reaction.

Reaction of cyclo*Hexene with Sulphur.*—(*a*) In a typical experiment, sulphur (0·3048 g.) and olefin (4·0582 g.) were heated at 139·3° for 5 hr.; the contraction in the dilatometer tube was 42 mm. The volatile portion (3·79 g.) of the mixture was unchanged olefin which was analytically (Found: C, 87·6; H, 12·2. Calc. for C_6H_{10}: C, 87·8; H, 12·2%) and spectroscopically pure but contained a trace of thiol (smell and darkening of lead acetate paper). The sulphurated residue (0·56 g.) [Found: C, 39·8; H, 5·5; S, 54·5%; *M* (ebullioscopic in C_6H_6), 367. Calc. for $(C_6H_{10}S_{3·1})_2$: C, 39·7; H, 5·5; S, 54·7%; *M*, 362] did not give a precipitate of sulphur even after one year at $-25°$. (*b*) Sulphur (2·0 g.), *cyclo*hexene (8·1 g.), and benzene (8·8 g.) were heated *in vacuo* at 150° for 6 hr. with gentle rocking. Evaporation *in vacuo* then gave a fraction of b. p. 79—80° (13·6 g.) and a yellow mobile oil (0·3 g.) (Found: C, 70·1; H, 9·8; S, 19·6%; C : H, 6 : 10). The residue (4·2 g.) (Found: C, 45·1; H, 6·7; S, 48·0; C : H, 6 : 10·6. Calc. for $C_{12}H_{20}S_5$: C, 44·5; H, 6·2; S, 50·8%) contained no phenyl groups as shown spectroscopically.

RESULTS

Until all the sulphur is consumed the sulphurated product can be formulated as two olefin units (RH) linked by several sulphur atoms, *i.e.*, $(RH)_2S_x$ (Table 1). The data are consistent with the product's being a mixture of alkenyl alkyl polysulphide, RS_xRH_2, and a polysulphide with two intermolecular sulphur linkages, $RH\underset{S_z}{\overset{S_y}{<}}RH$ ($x = y + z$), as revealed by structural studies.[2] During this period, to which the present kinetic study is restricted, the value of x remains sensibly constant, but it decreases thereafter, while the molecular complexity of the product increases, an effect which reflects the formation of a polymer species, $RS·[S_aRHS_b]_n·SRH_2$, which has also been identified earlier.[2]

Comparable data to those of Table 1 were obtained at 120° and 130°, indicating that the composition of the polysulphide is independent of temperature up to the stage of total combination of sulphur.

Calibration of Volume Contraction.—The linear contraction in the capillary tubing was

[4] Bacon and Fanelli, *Ind. Eng. Chem.*, 1942, **34**, 1043.
[5] Lyons and Watson, *J. Polymer Sci.*, 1955, **18**, 141.
[6] Cohen, Crosvos, and Sparrow, *J. Amer. Chem. Soc.*, 1950, **72**, 3947.

directly proportional to the amount of *cyclo*hexene which reacted, up to 5 hr. at 139·3° (Fig. 1),* as determined by the difference between the original and the recovered amounts of olefin. The amount of sulphur which reacted was deduced from the composition of the polysulphide

TABLE 1. *Composition of* cyclohexene *polysulphide* (139·3°).

Sulphur concn. (g.-atom/l.)	Time (hr.)	S atoms per *cyclo*hexene unit ($x/2$)	No. of *cyclo*hexene units in polysulphide molecule
1·6	1·5	3·5	2
1·6	2	3·5	2
3·2	2·3	3·7	2
3·2	4	3·4	2
0·8	5	3·2	2
1·6	5	3·1	2
3·2	5	3·1	2
3·2	6 *	2·9	2
1·6	7 *	2·3	2·2
1·6	49 *	0·9	2·5

* Sulphur totally combined.

produced and the amount of olefin which reacted. Since each polysulphide molecule contains two *cyclo*hexene units:

$$[P] = \tfrac{1}{2}[RH]_{changed} = \frac{1}{x}[S]_{changed} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where [P] is the concentration of polysulphide formed in mole/l., and RH and S denote the olefin and sulphur, respectively.
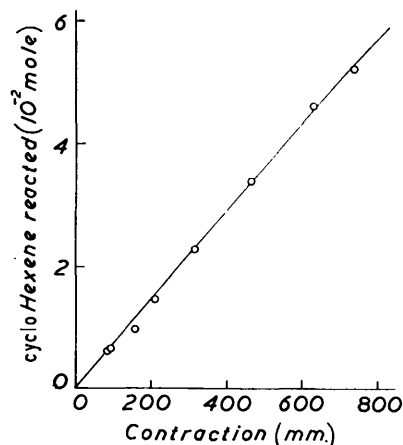

FIG. 1. *Relation between contraction in a* 1·5 *mm. diam. capillary and the amount of* cyclohexene *reacted.*

A similar relation applies for the other olefins studied.

Kinetic Study of the cycloHexene–Sulphur *Reaction at* 139·3°.—A typical run is shown in Fig. 2. During the first 2·5 hr. the rate increases to a maximum which persists for about 2 hr. and then diminishes until after 50 hr. the volume change becomes negligible. For the first 5 hr. the volume change reflects the formation of a polysulphide of approximately constant average composition (Table 1).

For the first tenth of reaction, the following relation was found to hold (Fig. 3 and Table 2):

$$[P]^{\frac{1}{2}} = k(t - t_i)[S]_0^{\frac{1}{2}}[RH]_0^{\frac{1}{2}} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where t represents total time, t_i an induction period, the suffixes indicate initial concentrations, and k is a proportionality constant. (Variation of $[RH]_0$ was achieved by using *cyclo*hexane as diluent.) The induction periods, t_i, increased with reductions in the sulphur and olefin concentrations and in temperature (*e.g.*, from *ca.* 0·05 hr. at 139·3° to 1·5 hr. at 115° for the

* In certain calibration experiments a dilatometer of 45 ml. capacity with a 4 mm. diameter capillary was used; in Fig. 1 the contraction given is for a 1·5 mm. diameter capillary.

TABLE 2. *Dependence of accelerating rate, r_a, on reactant and product concentrations* (139·3°).

[S]$_0$ (g.-atom/l.)	[RH]$_0$ (mole/l.)	$10^5 r_a$[P]$^{-\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{-\frac{1}{2}}$ sec.$^{-1}$)	$10^6 r_a$[P]$^{-\frac{1}{2}}$[S]$_0^{-\frac{1}{2}}$[RH]$_0^{-\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)
0·47	8·43	4·29	2·20
0·71	8·40	5·21	2·14
0·88	2·24	3·19	2·27
0·88	4·65	4·41	2·19
0·88	8·33	5·46	2·02
1·59	8·28	2·44	2·13
1·99	8·22	2·86	2·20
2·26	8·18	3·19	2·34
3·20	8·06	3·44	2·14

concentration conditions of Figs. 2 and 3), but definite correlations with these variables were not established.

FIG. 2. *Course of reaction of sulphur (2·0 g.-atom/l.) with cyclohexene (8·2 mole/l.) at 139·3°.*

O Experimental.
(————) Eqn. 10 ([RH] assumed constant).
(— — — — —) Change in [RH] allowed for.
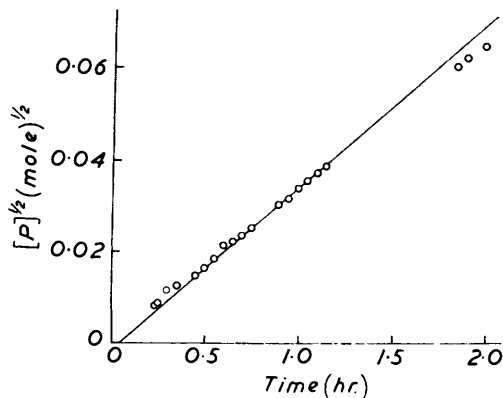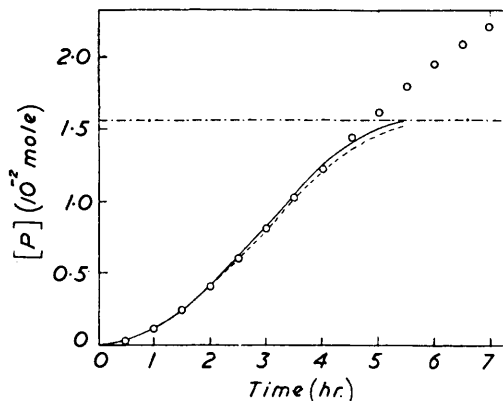(— · — · —) Limit of applicability of kinetic scheme.

FIG. 3. *Plot of square root of polysulphide formed against time during period of accelerative rate of the sulphur–cyclohexene reaction (reaction conditions as for Fig. 2).*

The rate in this accelerating period, r_a, is then given by:

$$r_a = d[P]/dt = 2k([P][S]_0[RH]_0)^{\frac{1}{2}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (3)$$

Precise correlation of the maximum rate, r_m, with the reactant variables has not been found possible. However, at the arbitrarily chosen time of half reaction, $t_{\frac{1}{2}}$, when [S]$_{reacted}$ = [S]$_0$/2 then the maximum rate, r_m, is found to be proportional to [S]$_0$ and to the square root of the concentration of olefin then present (Table 3), *i.e.*,

$$r_m = k'[S]_0([RH]_0 - [S]_0 x^{-1})^{\frac{1}{2}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

Effect of Temperature.—The relations (2), (3), and (4) also hold at 120° and 130°. From results at these temperatures and more limited results at 115° and 125° (Table 4), the Arrhenius

energies of activation for the reactions in the accelerating and the maximum rate regions were the same within experimental error (37 kcal./mole).

Effect of Additives.—" *cyclo*Hexene polysulphide " (Found: C, 54·2; H, 6·3; S, 48·5%) promoted the reaction and gave a constant rate in the early stages which was proportional to the square root of the concentration of the added polysulphide (Table 5).

TABLE 3. *Dependence of maximum rate, r_m, at $t_{\frac{1}{2}}$ on sulphur and cyclohexene concentrations (139·3°).*

$[S]_0$ (g.-atom/l.)	$[RH]_0$ (mole/l.)	$10^5 r_m$ (mole l.$^{-1}$ sec.$^{-1}$)	$10^6 r_m [S]_0^{-1} ([RH]_0 - [S]_0 x^{-1})^{-\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)
0·47	8·43	0·67	4·93
0·88	2·24	0·51	4·04
0·88	4·65	0·78	4·18
0·88	8·33	1·25	4·95
1·59	8·28	2·05	4·57
1·99	8·22	2·45	4·39
3·20	8·06	3·34	3·83

TABLE 4. *Temperature dependence of r_a and r_m.*

Temp.	115	120	125	130	139·3
$10^5 r_a [P]^{-\frac{1}{2}} [S]_0^{-\frac{1}{2}} [RH]_0^{-\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{3}{4}}$ sec.$^{-1}$)	0·136	0·216	—	0·725	2·22
$10^6 r_m [S]_0^{-1} ([RH]_0 - [S]_0 x^{-1})^{-\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{\frac{3}{4}}$ sec.$^{-1}$)	0·27	0·43	0·75	1·4	4·5

TABLE 5. *Effect of added cyclohexene polysulphide (P) on the cyclohexene–sulphur reaction at 120°. $[S]_0 = 0.49$ g.-atom/l.*

$[P]$ (mole/l.)	0·077	0·163	0·236
10^6 rate (mole l.$^{-1}$ sec.$^{-1}$)	1·46	2·07	2·46
10^6 rate $[P]^{-\frac{1}{2}}$	5·25	5·14	5·06

TABLE 6. *Effect of free-radical inhibitors on the sulphur–cyclohexene reaction.*

Free-radical inhibitor	Concn. (10^{-2} mole/l.)	Temp.	$10^5 r_a [P]^{-\frac{1}{2}} [S]_0^{-\frac{1}{2}}$ (sec.$^{-1}$)	Free-radical inhibitor	Concn. (10^{-2} mole/l.)	Temp.	$10^6 r_m [S]_0^{-1}$ (sec.$^{-1}$)
—	—	130°	2·1	—	—	120°	1·22
Quinol	12	130	2·1	Iodine	6·9	120	1·27
Benzoquinone	8·6	130	3·1	Diphenylpicryl-hydrazyl	0·25	120	0·6

Neither 1 : 1′-azo*iso*butyronitrile at 70° nor 1-azobis-1-phenylpropane at 110° appreciably affected the reaction.

Irradiation of the reaction mixture in a silica dilatometer with light from high- or low-pressure mercury lamps failed to induce reaction at 80—100°.

Typical inhibitors and retarders of free-radical chain reactions (Table 6) and of cationic polymerisations (*tert.*-butyl alcohol, pyridine, and dioxan) failed to retard sulphur–olefin reactions. On the contrary, iodine and diphenylpicrylhydrazyl eliminated the period of build-up to maximum rate, while benzoquinone increased r_a.

Trichloroacetic, benzoic, propionic, and stearic acid at 0·05—0·15M-concentrations increased the rate of reaction by 20—50% throughout its course, without affecting the composition of the product.

TABLE 7. *Effect of triethylamine on the sulphur–cyclohexene reaction.*

$[Et_3N]$ (mole l.$^{-1}$)	$[S]_0$ (mole l.$^{-1}$)	Temp.	$10^{-2} r_m [S]_0^{-1}$ (mm. hr.$^{-1}$ mole^{-1} l.)	$[Et_3N]$ (mole l.$^{-1}$)	$[S]_0$ (mole l.$^{-1}$)	Temp.	$10^{-2} r_m [S]_0^{-1}$ (mm. hr.$^{-1}$ mole^{-1} l.)
0	1·65	120°	1·2	0	1·69	135°	7·4
0·33	1·65	120	3·8	0·33	1·69	135	17·0

Triethylamine (0·33 mole l.$^{-1}$) at 120° and 135° decreased the time to reach, and gave a higher, maximum rate (Table 7), in agreement with earlier qualitative observations on amine catalysis of sulphur–olefin reactions.[7] The overall activation energy was reduced from 37 to 31 kcal./mole. During the period when the sulphur is not wholly combined, little change in product composition was detected.

Changing from cyclohexane as diluent to solvents of higher dielectric constant, viz., diethyl sulphide and nitromethane, increased the rate of reaction in this order (Fig. 4), without affecting the sigmoid nature of the extent of reaction–time curve. The product composition was unaffected, and there was no interaction of the sulphur with the solvent.

Although thiols have often been postulated as intermediates,[8,9] only traces have been detected in the products described in Parts VIII [2] and IX.[1] Addition of propane-2-thiol in concentrations from 1 to 50 molar % of the cyclohexene promoted the reaction at 130° without altering the shape of the reaction–time curve (Fig. 5). The increase in rate is not large, however, and does not indicate that the thiol is an active intermediate. Moreover, the volatile material recovered at the end of the reaction always contained unchanged thiol even after 25 hr. at 130°. In the polysulphidic product, isopropyl groups were detected spectroscopically and by the C : H ratio, but these could result wholly or in part from the ready exchange reaction between thiols and polysulphides.[10]

Reactions of Sulphur with Other Olefins.—The course of the reactions of sulphur with oct-1-ene, hept-2-ene, 1-methylcyclohexene, 2-methylpent-2-ene, 2 : 6-dimethyloct-2-ene, and 2 : 6-dimethylocta-2 : 6-diene simulates that with cyclohexene (Fig. 6). The reaction with 2 : 6-dimethyloct-2-ene has been studied in some detail, and kinetic characteristics similar in all respects to those reported above were observed. Equations (3) and (4) are obeyed (Table 8), and the energies of activation associated with the accelerative and maximum rates (38 and 37 kcal./mole, respectively; cf. Table 9) are practically identical with those found for cyclohexene. 1-Azobis-1-phenylpropane had no effect on the reaction, and the free-radical inhibitor tetra-

TABLE 8. *Reaction of sulphur with 2 : 6-dimethyloct-2-ene at 140°.*

[S]₀ (g.-atom/l.)	[RH]₀ (mole/l.)	$10^5 r_a[P]^{-\frac{1}{2}}[S]_0^{-\frac{1}{2}}[RH]_0^{-\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)	$10^6 r_m[S]_0^{-1}([RH]_0 - [S]_0 x^{-1})^{-\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)
0·49	4·70	3·05	6·9
0·57	0·45	3·05	6·8
0·57	0·92	3·22	6·0
0·57	2·23	3·02	6·6
0·57	3·14	2·94	6·6
0·77	4·68	3·18	7·3
1·10	4·65	3·11	7·3

TABLE 9. *Temperature-dependence of r_a and r_m for the sulphur–2 : 6-dimethyloct-2-ene reaction.*

Temp.	$10^5 r_a[P]^{-\frac{1}{2}}[S]_0^{-\frac{1}{2}}[RH]_0^{-\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)	$10^6 r_m[S]_0^{-1}([RH]_0 - [S]_0 x^{-1})^{-\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)	Temp.	$10^5 r_a[P]^{-\frac{1}{2}}[S]_0^{-\frac{1}{2}}[RH]_0^{-\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)	$10^6 r_m[S]_0^{-1}([RH_0]- [S]_0 x^{-1})^{-\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)
113·5°	0·11	0·28	130°	1·05	2·16
124·5	0·41	0·89	134·5	2·14	3·54
126·8	0·68	1·31	140	3·08	6·8

TABLE 10. *Reaction of sulphur with olefins at 140°.*

Olefin	$10^5 r_a[P]^{-\frac{1}{2}}[S]_0^{-\frac{1}{2}}[RH]_0^{-\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)	$10^6 r_m[S]_0^{-1}([RH]_0 - [S]_0 x^{-1})^{-\frac{1}{2}}$ (mole$^{\frac{1}{2}}$ l.$^{\frac{1}{2}}$ sec.$^{-1}$)	Composition of polysulphide
Oct-1-ene	1·6	4·1	$[C_8H_{16}S_{2\cdot4}]_{2\cdot2}$ *
2 : 6-Dimethylocta-2 : 6-diene	2·0	4·6	$[C_{10}H_{18}S_{3\cdot1}]_{2\cdot1}$
cycloHexene	2·3	4·9	$[C_6H_{10}S_{3\cdot1}]_{2\cdot0}$
Hept-2-ene	2·6	6·7	$[C_7H_{14}S_{2\cdot8}]_{2\cdot2}$
2 : 6-Dimethyloct-2-ene	3·1	6·8	$[C_{10}H_{20}S_{2\cdot5_3}]_{2\cdot1}$
2-Methylpent-2-ene	3·9	12·9	$[C_6H_{12}S_{2\cdot3_4}]_{2\cdot2}$
1-Methylcyclohexene	4·1	6·6	$[C_7H_{12}S_{2\cdot2_5}]_{2\cdot5}$

* For oct-1-ene the reaction time was 11 hr.; for other olefins this was 5 hr.

phenylhydrazine caused no retardation. The polysulphide product catalysed the reaction, as did dibenzyl tetrasulphide at 125°, the square of the rate being a linear function of the polysulphide concentration (Fig. 7).

[7] Moore and Saville, *J.*, 1954, 2082, 2089.
[8] Farmer and Shipley, *J. Polymer Sci.*, 1946, 1, 293.
[9] Bloomfield and Naylor, Proc. XIth Internat. Congress Pure Appl. Chem., 1947, Vol. II, p. 7.
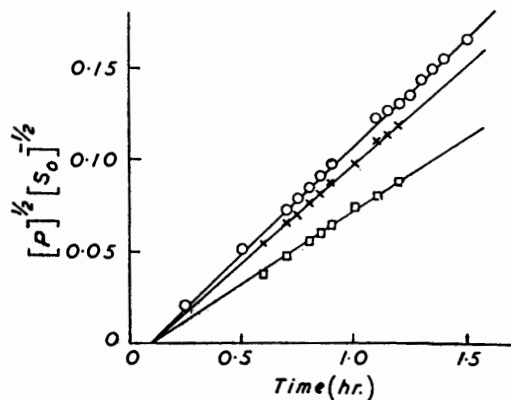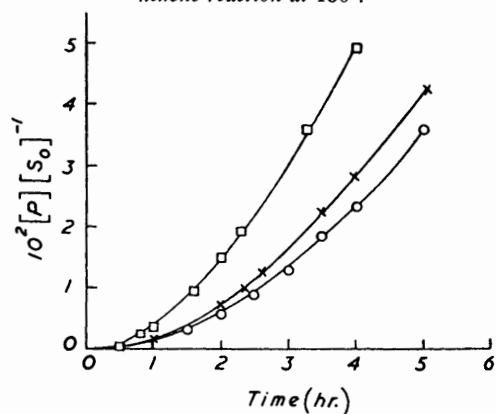[10] Birch, Cullum, and Dean, *J. Inst. Petroleum*, 1953, 39, 206.

FIG. 4.   *Effect of solvent medium on the sulphur–cyclohexene reaction at* 139·3°.

(—□—□—□—) *cyclo*Hexane, $\varepsilon = 2$ at 20°.
(—×—×—×—) Diethyl sulphide, $\varepsilon = 7\cdot2$ at 20°.
(—○—○—○—) Nitromethane, $\varepsilon = 39\cdot4$ at 20°.

FIG. 5.   *Effect of propane-2-thiol on sulphur–cyclohexene reaction at* 130°.

Thiol concn. (mole/l.):   (—○—○—○—), 0·0.
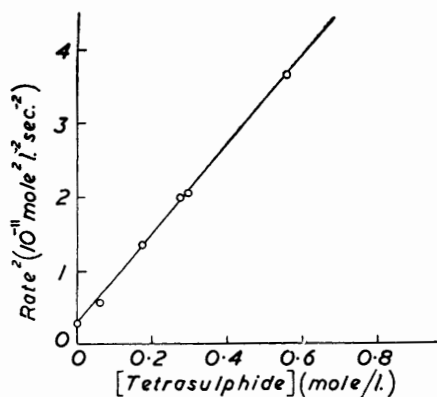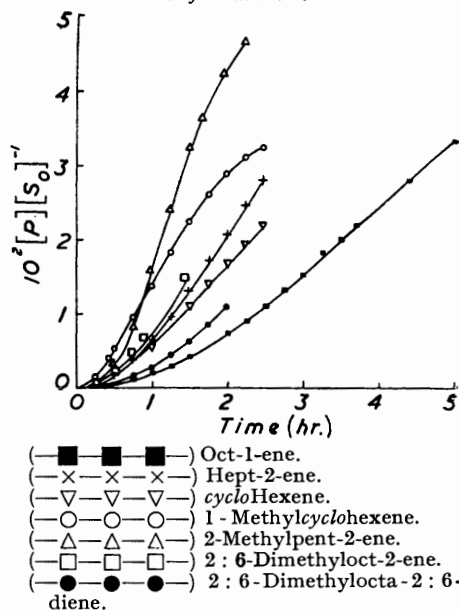(—×—×—×—), 0·26.   (—□—□—□—), 1·34.

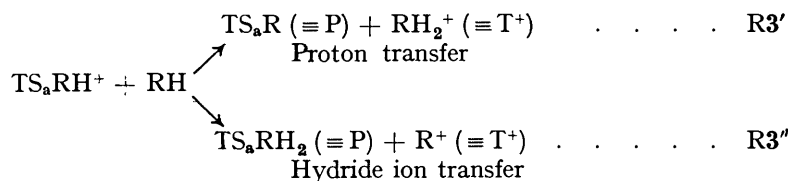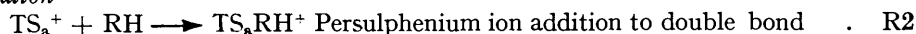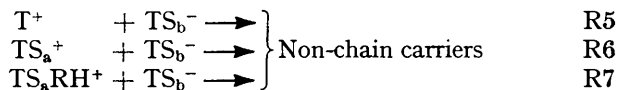FIG. 6.   *Course of reaction of sulphur with olefins at* 140°.

(—■—■—■—) Oct-1-ene.
(—×—×—×—) Hept-2-ene.
(—▽—▽—▽—) *cyclo*Hexene.
(—○—○—○—) 1-Methyl*cyclo*hexene.
(—△—△—△—) 2-Methylpent-2-ene.
(—□—□—□—) 2 : 6-Dimethyloct-2-ene.
(—●—●—●—) 2 : 6-Dimethylocta-2 : 6-diene.

FIG. 7.   *Effect of dibenzyl tetrasulphide on rate of reaction of sulphur with* 2 : 6-*dimethyloct-2-ene at* 125°.

Analysis of the rate measurements on the several olefins on the basis of equations (3) and (4) gives the data recorded in Table 10.

DISCUSSION

Olefin–sulphur interaction has been described as a free-radical chain process.[8,9] A polar rather than a free-radical mechanism is now indicated by (a) the non-retardation by substances which retard or inhibit known free-radical chain processes; (b) the non-catalysis by free-radical initiators and by ultraviolet light; (c) the catalysis by polar substances, especially amines and iodine; and (d) the increase in reaction rate in solvents of higher dielectric constant. The dependence of the accelerating rate, r_a, on the square root of the sulphur, olefin, and product concentration indicates a chain process in which the termination step involves mutual destruction of two chain carriers.

The annexed *formal* reaction scheme is proposed, which for convenience is restricted to the formation of the alkenyl alkyl polysulphide component of the reaction product.

Chain initiation
$$P \longrightarrow TS_a^+ + TS_b^- \qquad . \quad . \quad . \quad . \quad . \quad . \quad R1$$

Propagation
$$TS_a^+ + RH \longrightarrow TS_aRH^+ \text{ Persulphenium ion addition to double bond} \quad . \quad R2$$

$$TS_aR \;(\equiv P) + RH_2^+ \;(\equiv T^+) \qquad . \quad . \quad . \quad . \quad R3'$$
Proton transfer

$$TS_aRH^+ + RH$$

$$TS_aRH_2 \;(\equiv P) + R^+ \;(\equiv T^+) \qquad . \quad . \quad . \quad . \quad R3''$$
Hydride ion transfer

$$T^+ + S_8 \longrightarrow TS_a^+ \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad R4$$

Termination

$$\left.\begin{array}{l} T^+ \qquad + TS_b^- \longrightarrow \\ TS_a^+ \qquad + TS_b^- \longrightarrow \\ TS_aRH^+ + TS_b^- \longrightarrow \end{array}\right\} \text{Non-chain carriers} \qquad \begin{array}{l} R5 \\ R6 \\ R7 \end{array}$$
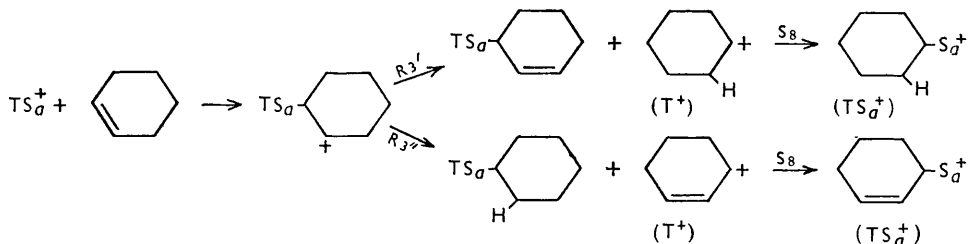
It will be shown in the following paper that the other main products of mono-olefin sulphuration which have been revealed by the structural studies reported in Part VIII[2] can be explained by rational and kinetically equivalent variants of the propagation steps R2—R4.

Three basic features of the mechanism require comment. First is the heterolysis of an S–S bond as the initiation step, rather than a homolysis as previously supposed.[8,9] This is a novel postulate, but is not at variance with present knowledge of the reactivity of S–S bonds in sulphur and polysulphides.[11] Secondly, the chain carriers are identified with cations, although a kinetically similar mechanism can be based on participation of the persulphenyl anion in the propagation. This choice is based (i) on the known susceptibility of " non-activated " double bonds to electrophilic attack, and their resistance to nucleophilic reagents,[12] and (ii) on the structures of the products. Thirdly, although the intermediates are formulated as ions, it is not imagined that these exist as such in the reaction environment, but rather that highly polarised molecules and ion pairs or aggregates are formed which react with the ionic character specified. All three features are of considerable general interest and justify a fuller discussion which is given in the following paper.

[11] Bateman, Moore, and Porter, following paper.
[12] Dewar, " The Electronic Theory of Organic Chemistry," Oxford Univ. Press, 1949, p. 142.

Application of the formal scheme to *cyclo*hexene indicates how a product having an average alkenyl alkyl polysulphide structure is formed:

$$TS_a^+ \;+\; \bigcirc\!\!=\; \longrightarrow \; TS_a\!-\!\bigcirc \;\overset{R3'}{\longrightarrow}\; TS_a\!-\!\bigcirc\!\!=\; +\; \bigcirc\!\!-\!H \;(T^+)\; +\; \overset{S_8}{\longrightarrow}\; \bigcirc\!\!-\!S_a^+\;H \;(TS_a^+)$$

$$\overset{R3''}{\longrightarrow}\; TS_a\!-\!\bigcirc\!\!H \;+\; \bigcirc\!\!=\; (T^+)\; +\; \overset{S_8}{\longrightarrow}\; \bigcirc\!\!=\!S_a^+ \;(TS_a^+)$$

In this case the kinetically equivalent reactions R3' and R3'' yield structurally identical products and thus no means is available to determine their relative participation. With olefins having unsymmetrically substituted double bonds, however, structurally distinct polysulphides will result from the occurrence of R3' and R3'' and thus their relative importance for these olefins can be deduced. The relative rates of reaction among the mono-olefins (Table 10) are consistent with increase in nucleophilic power and facilitation of reaction R2 by increased alkyl substitution at the double bond. The variation in rate is small, however, probably in part owing to some compensating change of reactivity in the other chain carriers (TS_aRH^+ and T^+) and in part because of the much larger contribution of the initiation reaction, R1, to the overall energetics of the reaction.

Kinetic Requirements of the Reaction Mechanism.—By assuming stationary-state conditions and long kinetic chains, the following rate equation is derived:

$$r^{-2}[P][S][RH] = A^{-1}[S]^{-1}x^2[RH] + B^{-1}x + C^{-1}[S][RH]^{-1} \qquad . \quad . \quad (5)$$

where
$$r = d[P]/dt = -\tfrac{1}{2}\,d[RH]/dt = -\frac{1}{x}\,d[S]/dt \quad . \quad . \quad . \quad . \quad (6)$$

$$A^{-1} = k_1^{-1}k_4^{-2}k_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$B^{-1} = (k_5 + k_6)k_1^{-1}k_2^{-1}k_4^{-1} + (k_5 + k_7)k_1^{-1}k_3^{-1}k_4^{-1} \quad . \quad . \quad . \quad (8)$$

$$C^{-1} = k_1^{-1}(k_2^{-1}k_6 + k_3^{-1}k_7)(k_2^{-1} + k_3^{-1}) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and reactions R3' and R3'' are treated as a composite reaction R3.

Equation (5) is seen to be equivalent to the experimentally determined rate in the accelerating region (equation 3) provided A^{-1} and C^{-1} are neglected. This condition holds if the reactions involving the hydrocarbon ion T^+ are either very much faster or slower than the reactions involving the other intermediates. The former case is supported indirectly by the fact that benzene does not participate in the reaction (p. 2857). An interesting consequence of the greater reactivity of the T^+ species is apparent experimentally in the 2 : 6-dimethylocta-2 : 6-diene reaction (see below).

During the early stages of the reaction when [RH] is practically constant, integration of equation (5) (terms in A and C being neglected) gives:

$$2x[P] = [S]_0[1 - \cos(B[RH]_0)^{\frac{1}{2}}t] \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Expressing $\cos(B[RH]_0)^{\frac{1}{2}}t$ as a power series and ignoring powers of t greater than the second then leads to:

$$[P] = B[S]_0[RH]_0t^2/4x \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which is identical with equation (2) if $2k = (B/x)^{\frac{1}{2}}$.

The theoretical rate in the accelerating period is therefore given by:

$$r_a = (B/x)^{\frac{1}{2}}([P][S]_0[RH]_0)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

By choosing the time in the region of maximum rate where half the sulphur reacts and substituting the appropriate polysulphide and olefin concentrations then obtaining

{*viz.*, $[S]_0/2x$ and $([RH]_0 - [S]_0x^{-1})$, respectively} into equation (5), and again neglecting terms in A and C, gives the theoretical maximum rate at $t_{\frac{1}{4}}$ as:

$$r_m = B^{\frac{1}{2}}[S]_0([RH]_0 - [S_0]x^{-1})^{\frac{1}{2}}/2x \quad . \quad . \quad . \quad . \quad (13)$$

This is identical with the experimental expression (equation 4), with $k' = B^{\frac{1}{2}}/2x$.

From the found values of k and k', B and x can be separately evaluated, as for *cyclo*-hexene in Table 11. On substituting these into equation (10), then the full lines in Figs.

TABLE 11. *Theoretically derived value of B and x for the sulphur–cyclohexene reaction.*

Temp.	115°	120°	130°	139·3°
$10^5 B^{\frac{1}{2}}$ (mole$^{-\frac{1}{2}}$ 1.$^{\frac{1}{2}}$ sec.$^{-1}$)	0·29	0·55	1·9	5·5
x	6·4	6·4	6·7	6·0

2 and 8 give the course of the reaction. Agreement with the experimental points is good until 90% of the sulphur has reacted and is further improved by correcting for the change in olefin concentration (broken lines). The values of x determined in this way agree well with experiment (cf. Table 1).

FIG. 8. *Course of reaction of sulphur (2·0 g.-atom/l.) with cyclohexene at 120° and 130°.*

☐ Experimental at 120°.
○ Experimental at 130°.
(————) Eqn. 10 ([RH] assumed constant).
(— — — —) Change in [RH] allowed for.
(—·—·—) Limit of applicability of kinetic scheme.
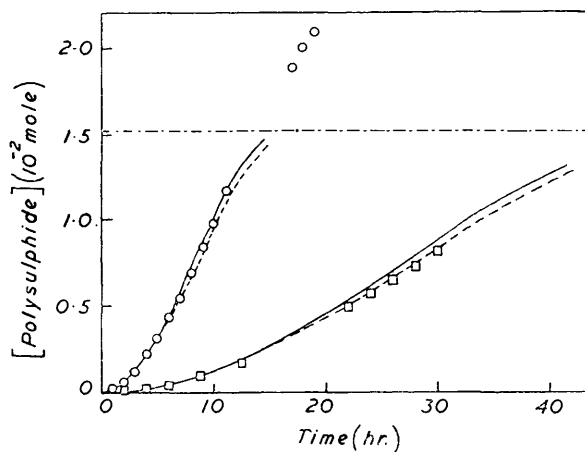
Although equations (5), (12), and (13) have been derived on the assumption of long kinetic chains, this assumption is superfluous if termination occurs solely by reaction R6 (the reverse of the initiation reaction) since rate equations of the same form then result.

The mechanism tacitly assumes that polysulphide is present initially to undergo dissociation to produce a chain carrier, but this is not so. A direct reaction between sulphur and the olefin must therefore precede the chain process, rapidly becoming relatively insignificant as polysulphide is formed. The occurrence of induction periods at the lower temperatures studied and at lower sulphur and olefin concentrations (p. 2858) is consistent with both reactants' engaging in a prior reaction of this kind which proceeds far less readily than the later multistage interaction. The influence of promoters of the overall reaction appears informative in this sense. One class, *e.g.*, acids, do not affect the sigmoid nature of the reaction–time curve and appear to facilitate the propagation reactions, probably by aiding the proton exchange process R3′. Another class, *e.g.*, iodine, amines, and 2 : 2-diphenyl-1-picryhydrazyl, gives an enhanced and initially linear rate of reaction, almost certainly by reacting or forming complexes with the sulphur to give polarised persulphenyl species more readily than does the olefin by direct reaction.[11]

Cyclic Sulphide Formation in the 1 : 5-*Diene System.*—An apparently anomalous feature of the comparative rates of reaction of different olefins (Table 10) is that 2 : 6-dimethyl-octa-2 : 6-diene reacts more slowly than a strictly comparable mono-olefin (2 : 6-dimethyl-oct-2-ene) despite having twice the concentration of double bonds as reactive sites. This diene also differs from mono-olefins in yielding a cyclic monosulphide mixture as a major

product.[1]   These two features now appear to be related and to reflect a special variant of the reaction mechanism in 1 : 5-diene systems, *viz.*, interaction of an S–S bond of a polysulphide, formed as outlined above, with a carbonium ion formed at an adjacent double
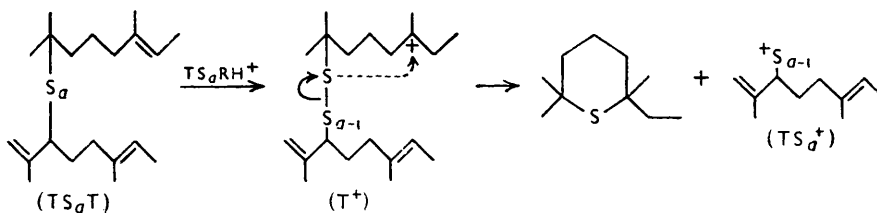
bond by prior proton-transfer with TS_aRH^+, as illustrated.   The essential kinetic feature of this process is that the carbonium ion (T^+) is transformed into a cyclic sulphide and the less reactive chain carrier TS_a^+ without consuming elemental sulphur.   By thus explaining the reduced rate of reaction, as well as exactly defining the cyclic sulphides formed, strong evidence for the validity of the proposed formal mechanism is provided.

The author is indebted to Dr. L. Bateman and Dr. C. G. Moore for guidance during the course of this work and for much assistance in preparing this paper for publication.