298. The Radiation Chemistry of β-Pinene.

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On irradiation with cobalt-60 γ-rays, dry β-pinene polymerizes *in vacuo*, to give a product which is partially precipitated from the liquid monomer. The kinetics of the reaction have been followed by using dilatometers. At 25—30° with a constant dose rate (2.55×10^{17} ev g.$^{-1}$ min.$^{-1}$), polymer formation is linear with time of irradiation up to 60% conversion and the mean yield corresponds to the polymerization of 850 monomer molecules per 100 ev. A decrease in dose rate results in a higher yield per unit dose. The rate shows a positive temperature coefficient in the range −35° to +55°. The polymers are formed with a range of molecular weights and a number-average value of 1360 is obtained for the chloroform-soluble fraction; the insoluble polymer is of higher molecular weight and melts at 220°. Infrared and nuclear magnetic resonance spectra together with the determination of iodine values indicate the presence of unsaturated groups in the polymer structure. The polymerization yield is sensitive to the drying technique employed for the monomer and the rate of a dry reaction is strongly retarded by added water although the molecular weight of the resultant polymer is unaffected. Evidence of initiator transfer to monomer during the dry polymerization, as well as the marked effect of water, strongly support the participation of ions in the mechanism. A concurrent isomerization of β-pinene to dipentene ensues during the polymerization with a yield of 12 molecules per 100 ev; other isomers are also formed in comparable yields.

CHEMICAL changes undergone by β-pinene (I) under the influence of heat and catalysts are often accompanied by rearrangements of the bicyclic ring structure. Thermal decomposition [1] at >200° is analogous to that sustained by α-pinene and leads to myrcene (II) and dipentene (III) by the complete and partial disruption, respectively, of the bicyclic

(I)   (II)   (III)   (IV)
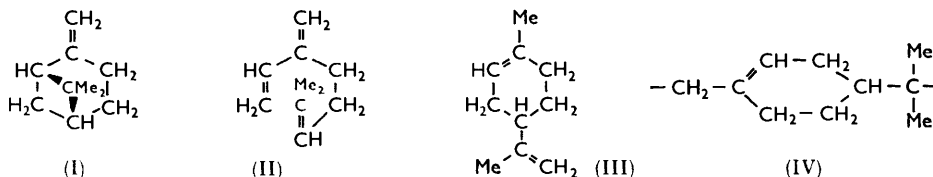
system. It has been suggested [2] that the thermal isomerization involves a biradical intermediate. Acid-catalysts of the Friedel–Crafts type react with β-pinene to form homopolymers of low molecular weight [3] and it has recently been shown [4] that a similar polymer is formed by the use of a Ziegler catalyst. Although these polymers probably contain more than one type of structure in the repeating unit, it is considered probable [3,4] that the main contribution is represented by (IV) and involves the opening of the bicyclic bridge structure. There is little doubt that these polymerizations are of the cationic variety [5] and proceed by rearrangement of a carbonium ion before each addition step according to a Wagner–Meerwein transformation.[6]

The present investigation was initiated to compare the effects of ionizing radiation with the above changes. Since ions and radicals are the postulated intermediates in the radiation chemistry of organic compounds,[7] it is of interest to examine the products in

[1] Frost and Pearson, " Kinetics and Mechanism," J. Wiley and Sons, Inc., New York, 1961, p. 373.
[2] Burwell, *J. Amer. Chem. Soc.*, 1951, **73**, 4461.
[3] Roberts and Day, *J. Amer. Chem. Soc.*, 1950, **72**, 1227.
[4] Marvel, Hanley, and Longone, *J. Polymer Sci.*, 1959, **40**, 551.
[5] Schildknecht, " High Polymers," Interscience Publ., Inc., New York, 1956, Vol. X, p. 203.
[6] Barton and Harper, " Chemistry of Carbon Compounds," Elsevier Publ. Co., Amsterdam, 1953, Vol. IIb, p. 573.
[7] Swallow, " Radiation Chemistry of Organic Compounds," Pergamon Press Ltd., London, 1960, p. 11.

relation to the effects brought about by reagents that are specifically known to react by either ionic or radical processes. In this manner it is possible to integrate the classification of radiation-induced changes into the established pattern of reaction mechanism in organic chemistry. A preliminary account of this work has been published;[8] no other work has hitherto been described in the literature on the irradiation of pure β-pinene, although the irradiation of a mixture of carbon tetrachloride and β-pinene is reported[9] to give the 1 : 1 addition product similar to that formed in the reaction initiated by thermal decomposition of benzoyl peroxide.[10]

<div align="center">EXPERIMENTAL</div>

Materials.—β-Pinene, supplied by L. Light and Co. Ltd., was fractionally distilled at 30 mm. through a 200-cm. column packed with stainless-steel gauze spirals. The fractions were analysed by gas–liquid chromatography as described in the preceding paper.[11] In the more volatile fractions, appreciable quantities of α-pinene were identified but after more than half the original batch had been distilled off, the remaining distillate was rich in β-pinene, with a total content of other isomers estimated at less than 1%. This material was stored in a refrigerator and further distilled from copper stearate immediately before use in irradiation experiments.

Silica gel (from B.D.H. Ltd.), graded for chromatographic purposes, was activated by heating it at 250° for 2—3 hr. and transferred to a desiccator. It was left for 2—4 days before use as a drying agent. Other drying methods used in this work depended on storing the monomer over sodium, magnesium perchlorate, phosphorus pentoxide, and calcium hydride; these materials were of the best available grade and were used without further purification. Molecular sieve (type 4A), supplied by B.D.H. Ltd., and manufactured by Linde Air Products Company, U.S.A., was also employed for dehydrating the monomer in some experiments.

Triply distilled water, free from organic impurities, and 99·7% deuterium oxide were used as sources of water vapour to determine the effect of water on the radiation-induced reaction.

Apparatus and Procedure.—The earliest experiments were carried out in vacuum-sealed tubes, and the extent of reaction was determined at the end of a run. In order to obtain kinetic data, the progress of the polymerization was followed in dilatometers. A full account of the filling technique and the procedures for the addition of water have been given.[12] Volume contractions in the dilatometer were measured at 25° irrespective of irradiation temperature.

Monomer samples were irradiated in two cobalt-60 sources. Within a 400-c annular source, the uniform dose rate region corresponded to an energy input of $2·55 \times 10^{17}$ ev g.$^{-1}$ min.$^{-1}$. At a fixed location from a 1-c cylindrical source, the dose rate was $4·58 \times 10^{15}$ ev g.$^{-1}$ min.$^{-1}$. Measurements of energy absorption are based on the use of the Fricke dosimeter with $G(Fe^{2+}$ ions oxidised/100 ev) taken to be 15·6; the change in electron density from 0·8N-sulphuric acid to pinene is allowed for in the above values. In the larger source the temperature of the sample was regulated above ambient by placing the dilatometer in a jacketed heating-coil; temperatures below ambient were reproduced by inserting the cell into a Dewar flask containing a liquid (water or acetone) cooled to the desired temperature.

Polymer Estimation and Analysis.—After irradiation, the dilatometer cell was opened and emptied; the insoluble polymer was removed from the glass walls by agitation with a glass rod and rinsing with chloroform. Thereafter, the total contents were treated with 6 volumes of methanol to precipitate the total polymer, which was centrifuged off and then dried *in vacuo* at 100° to constant weight; evaporation of the methanol filtrate yielded a gum which amounted to only a few per cent of the total precipitated polymer. The total polymer was refluxed with " AnalaR " chloroform in a nitrogen atmosphere and the insoluble portion separated; the soluble fraction was re-precipitated with methanol and isolated as before.

The infrared spectra of the polymer fractions were measured on compressed potassium

[8] Bates and Williams, *Nature*, 1960, **187**, 665.

[9] Webb, Proc. Second U.N. Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. XXIX, p. 331.

[10] Oldroyd, Fisher, and Goldblatt, *J. Amer. Chem. Soc.*, 1950, **72**, 2407.

[11] Bates, Best, and Williams, preceding paper.

[12] Best, Bates, and Williams, *Trans. Faraday Soc.*, 1962, **58**, 192.

bromide discs containing about 1% of the polymer by means of a Hilger H 800 double-beam instrument Nuclear magnetic resonance measurements on a saturated solution of polymer in carbon tetrachloride were carried out by Dr. R. E. Richards at the Physical Chemistry Laboratories, Oxford University. Determinations of unsaturation in the polymer were effected by the estimation of iodine values according to standard procedures.[13] Also, a solution of the polymer in benzene was treated with a palladium catalyst and hydrogen at room temperature; the hydrogen uptake was measured and the polymer reprecipitated from solution.

The m. p.s of the polymer fractions were obtained by using a micro-heating-block but the molten polymer became yellow on exposure to air; polymer samples in evacuated glass phials could be melted and cooled repeatedly at $>200°$ without changing colour or infrared spectrum. A sample of total polymer has a m. p. in the range 180—190°.

TABLE 1.

Melting points of polymer fractions.

	Conversion into polymer (wt. %)	Polymer sol. in $CHCl_3$ (wt. %)	Melting points	
Run no.			$CHCl_3$-sol. fraction	$CHCl_3$-insol. fraction
68	5·6	62	150—152°	215—235°
36	17	85	150—179	208—224
69	38	74	150—152	220—235
37	44	84	150—161	210—224
35	57	82	130—150	190—215
34	59	85	—	—

In earlier work, the polymer which was precipitated from the monomer was isolated separately. For two runs in which the total conversions of monomer into polymer were 54% and 79%, the respective fractions of polymer precipitated from the monomer were 0·32 and 0·56. This precipitated material had a m. p. in the range 200—238° whereas the polymer soluble in the monomer had a much lower m. p. (between 80° and 105°). Polymer precipitated from the monomer and subsequently heated to melting *in vacuo* had: C, 88·4, 88·1; H, 11·6, 11·6%, in separate determinations [Calc. for $(C_{10}H_{16})_n$: C, 88·2; H, 11·8%]. Analytical agreement is satisfactory. If samples of methanol-precipitated polymer were left in air for several days before analysis, an appreciable discrepancy appeared in the analytical results; this was due to partial oxidation, as confirmed by infrared spectrum which showed the growth of absorption at $5·8\,\mu$ (C=O). The density of the total polymer was determined by the displacement technique, with methanol as fluid; in a run carried to 59% conversion, a density of 1·052 was obtained. Molecular-weight determinations were made by an ebulliometric method.[12]

Determination of Isomerization.—A different procedure in handling the sample after irradiation was followed to enable the liquid monomer to be analysed. The contents of the irradiation cell were transferred to a tube which was attached to a vacuum-line and evacuated; the monomer was distilled slowly from the polymer into a receiver at $-196°$, the final traces being removed by magnetic stirring of the solid–liquid mixture. Analyses of this distillate together with the control samples, as retained from the cell-filling operation before irradiation, were made by the gas–liquid chromatographic method described before.[11]

Gas Analysis.—The technique was identical with that used in the similar study of α-pinene.[11]

RESULTS AND DISCUSSION

Kinetics.—Early experiments on β-pinene which had been dried with calcium hydride and irradiated in vacuum-sealed tubes gave poor reproducibility of polymer formation as a function of dose. The effect of different drying agents in the pre-treatment of the monomer is illustrated in Table 2; the polymer yield is calculated on the basis of the polymer determination at the end of the run; runs refer to ambient temperature in the source (25—30°) unless otherwise stated.

It is apparent that the polymer yield is depressed by the presence of water and that different drying agents differ in their ability to promote the polymer yield. The passage

[13] Jacobs and Scheflan, " Chemical Analysis of Industrial Solvents," Interscience Publ., Inc., New York, 1953, p. 62.

TABLE 2.

Effects of drying agents on polymerization yield.

Run	Drying method	Conversion into polymer (wt. %)	$G(-\text{monomer})$ (molecules/ 100 ev)	Run	Drying method	Conversion into polymer (wt. %)	$G(-\text{monomer})$ (molecules/ 100 ev)
17	Na	2·9	22	24	P_2O_5	1·8	31
18	CaH_2	1·8	51	26	Al_2O_3	23·0	370
20	None: satd. with H_2O	3·4	6	36	SiO_2 *in vacuo*	16·6	2230
				34	SiO_2 *in vacuo*	59·0	1050

of the liquid monomer down a 10—20 cm. column of silica gel *in vacuo* gives the highest polymerization yields. However, when silica gel or sodium aluminium silicate (molecular sieve 4A) was highly activated in the vacuum-system, isomerization of the β-pinene occurred on subsequent contact and afforded about 20% of α-pinene, camphene, and dipentene. Since it was desirable to conduct the irradiations on β-pinene of the highest purity and at the same time eliminate water as effectively as possible, a compromise procedure was used whereby the monomer was passed down a 10 cm. column of aged silica gel before its entry into the vacuum-apparatus.[12] The monomer was distilled *in vacuo* before the irradiation cell was filled; thus any polymer formed by treatment with silica gel remained in the
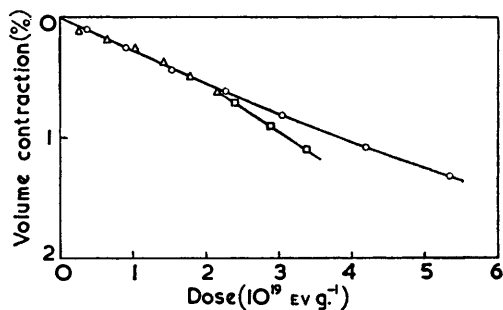

FIG. 1. Influence of temperature on rate of polymerization.

Run (a) ○ at 25°. Run (b) △ at 25°.
□ at 55°.

distillation flask. Unirradiated samples of monomer showed only 1—2% of other isomers. Use of the latter drying technique allowed the polymerization kinetics to be measured in a series of dilatometer runs. A linear relation was satisfied between total volume contraction at the end of a run and polymer conversion; the shrinkage factor corresponds to 5·45% of polymer per 1% volume contraction. A typical contraction curve shown in Fig. 1 illustrates the general kinetic behaviour. Apart from a slight induction period for an initial dose of less than $2·5 \times 10^{18}$ ev/g., whereafter the rate * accelerates to a steady value, polymer production remains linear with dose up to 60% conversion. At higher conversions the rate declines. The linear portions of the contraction curves are used to obtain the absolute yields. Calculation of the mean yield at 25° from the results of 14 runs gives $G(\text{-monomer})$ 849 ± 225 (standard deviation) whereas, if only the 6 highest yields are selected, the average $G(\text{-monomer})$ is 1086 ± 78. These values refer to a dose rate of $2·47 \times 10^{17}$ ev g.$^{-1}$ min.$^{-1}$.

The kinetic effects due to changes in temperature, dose rate, and addition of water were evaluated by changing the conditions [12] after the steady polymerization rate referred to above had been attained; because of the uncertainty in yield from run to run, this is considered more reliable for comparison than carrying out separate runs under each set of conditions. In regard to changes of either irradiation temperature or dose rate, the rate undergoes a sharp transition from one value to another as illustrated in Fig. 1. The results are summarized in Tables 3 and 4.

The dependence of rate on the temperature between 0° and 55° corresponds to an activation energy of 1·4 kcal./mole whereas the results at 0° and —35° give a value of 2·8

* Rate is per unit of dose unless otherwise stated.

TABLE 3.

Temperature-dependence of polymerization rate.

(Dose rate 2.47×10^{17} ev g.$^{-1}$ min.$^{-1}$.)

Temp. (K)	238°	273°	298°	328°
$10^3/T$	4·20	3·66	3·36	3·05
R (Rate in arbitrary units)	3·9	8·2	10·0	12·4
ln R	1·36	2·10	2·30	2·52

TABLE 4.

Dependence of polymerization rate on dose rate at ~25°.

Position a, 2.55×10^{17} ev g.$^{-1}$ min.$^{-1}$; position b, 4.58×10^{15} ev g.$^{-1}$ min.$^{-1}$.

Run no.	Rate per unit dose [volume contraction (%) per ev g.$^{-1}$]		(R_b/R_a)
	position a	position b	
48	2.32×10^{-20}	3.58×10^{-20}	1·54
49	3.00×10^{-20}	4.21×10^{-20}	1·40
51 *	1.19×10^{-20}	1.93×10^{-20}	1·62

* Molecular sieve as drying agent.

kcal./mole. A lower dose rate appears to favour a higher yield or rate per unit dose; the results in Table 4 may also be adequately expressed by the statement that the rate of polymerization per unit time is proportional to the (dose rate)$^{0.9}$.
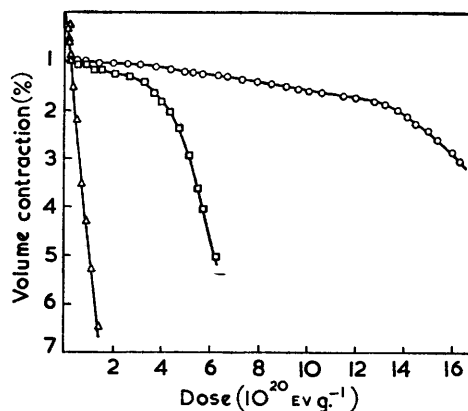

FIG. 2. Effect of addition of water on rate of polymerization.

Dose rate 2.53×10^{17} ev g.$^{-1}$ min.$^{-1}$. △, Water absent. □, 5.38×10^{-3}M-H_2O. o, 1.15×10^{-2}M-H_2O.

As discussed earlier in relation to the results of Table 2, the addition of water to the monomer results in a much lower overall polymerization yield. Some kinetic details are represented in Fig. 2, which includes a run in total absence of water. The water was added after the polymerization had been followed in each case to about 1% volume contraction. The polymerization curve diverges considerably from the initial rate obtained in the absence of water. Thereafter, polymerization accelerates and attains a constant maximum rate after a dose which depends on the amount of added water. We define this induction dose as the dose at the intercept of the extrapolated maximum rate on the ordinate corresponding to the point of addition, minus the initial dose given in the anhydrous state. G_i and G_f refer to the polymerization yields after the initial addition of water and to the final constant rate, respectively. $G(-H_2O)$ is calculated on the assumption that the added water concentration is completely consumed in the irradiation period corresponding to the induction dose. The results are in Table 5. Despite the acceleration of rate after addition of water, G_f does not attain the polymerization yield characteristic of the dry system. The proportionality between the induction dose and the concentration of added water is reflected in the relative constancy of $G(-H_2O)$.

TABLE 5.

Kinetic data in the presence of water.

$10^3[H_2O]$ (M)	G_i −monomer (molecules/100 ev)	G_t (molecules/100 ev)	Induction dose $(10^{20}$ ev g.$^{-1})$	$G(-H_2O)$ (molecules/100 ev)
2·39	36·2	333	1·6	1·04
4·0 (D$_2$O)	6·0	420	3·19	0·87
5·38	28·4	458	3·9	0·96
11·5	6·4	98	11·0	0·73
satd.	6·4	183	—	

Although the main radiation-induced reaction is polymerization, a concurrent iso-merization was also measurable. Dipentene is formed with a *G* yield of 12 over a range of polymer formation from 6 to 40% conversion of monomer; two other unidentified isomers are produced with comparable yields (*G ca.* 10). The formation of gaseous products represents only an insignificant part of the chemical change in this system. Thus after an irradiation involving 89% conversion into polymer, the evolved gas volatile at −196°, presumably hydrogen and methane, corresponds to a *G* value of 0·7; also the *G* value for C$_2$ products was less than 0·1.

Molecular Weights and Constitution of the Polymer.—The molecular weights of the polymer fractions were measured in chloroform. Hence it was necessary to have material which readily dissolved and this was obtained by a pre-extraction of the total polymer with different solvents; no information is presented on the molecular weights of the chloroform-insoluble fractions. The determinations are recorded in Table 6.

TABLE 6.

Molecular weights of soluble polymers.

| Run no.	Conversion into polymer (wt. %)	Extraction solvent	Mol. wt. ($\bar{M}_n$)	Run no.	Conversion into polymer (wt. %)	Extraction solvent	Mol. wt. ($\bar{M}_n$)
68	5·6	CHCl$_3$	1220 ± 20	66	17·5	CCl$_4$	1410 ± 71
35	57·0	,,	1395 ± 56	66	17·5	C$_6$H$_6$	1300 ± 85
37	43·9	,,	1450 ± 70	66 [b]	17·5	,,	1110 ± 50
53 [a]	33·0	,,	1840 ± 180	9	3·2	β-Pinene monomer	570 ± 8
56	64·0	CCl$_4$	1285 ± 39	3	54·0	,, ,,	494 ± 15

[a] Water-satd. run.   [b] Hydrogenated polymer.

Although water has a profound effect on the polymerization rate, it is apparent from Table 6 that the molecular weight of the polymer is not reduced in consequence, as in a similar study on α-methylstyrene.[12] The highest molecular weights of the β-pinene polymers obtained with a Friedel–Crafts catalyst [3] are somewhat higher (*ca.* 3000) than the values recorded here; nevertheless, the Friedel–Crafts polymer is completely soluble in the monomer, whereas the radiation-induced polymer is partly insoluble and probably contains additional material of higher molecular weight. It is likely that these differences arise from a narrower molecular-weight distribution in the Friedel–Crafts polymer. The difference in molecular weights between the two fractions of radiation-induced polymer which are soluble in chloroform and β-pinene, respectively, suggests that a large amount of material of low molecular weight is present in the total polymer. There is no evidence from Table 6 that the molecular weights of the chloroform-soluble fractions depend upon the percentage conversion into polymer. Some notable differences are evident between the infrared spectra of the radiation-induced and Friedel–Crafts polymers illustrated in Fig. 3. The strong band at 12·7 μ in the Friedel–Crafts sample is characteristic of the grouping CRR″:CHR″ and by analogy with the spectrum of α-pinene can be assigned to the double bond in the cyclohexane ring of structure (IV); this band is in general con-siderably weaker in the radiation-induced polymer, although in some samples it was

stronger than in the spectrum shown in Fig. 3. A considerable number of well-defined absorption bands are present in the radiation-induced polymer which are absent in the other polymer; in particular these are medium-to-strong bands at 6·96, 7·64, 10·26, 10·98, 12·08, and 13·60 μ. The strong band at 10·98 μ is consistent [14] with the presence of a vinyl group, and the bands at 12·1 and 13·6 μ could be due to various forms of trisubstituted unsaturated groups. The radiation-induced polymer produced in a water-saturated run shows an extra band at 11·2 μ in addition to the bands observed in the polymers formed under dry conditions; this strongly indicates the additional presence of a vinylidene group, $CRR'':CH_2$. The infrared spectrum of a sample of radiation-induced polymer which had been recovered after bromination in chloroform solution showed considerable changes from that of the original material but the elimination of the band at 10·98 μ

FIG. 3. Infrared spectra of polymers (KBr disc).

1, Radiation-produced.
2, Commercial.
3, H_2O present.
4, D_2O present.
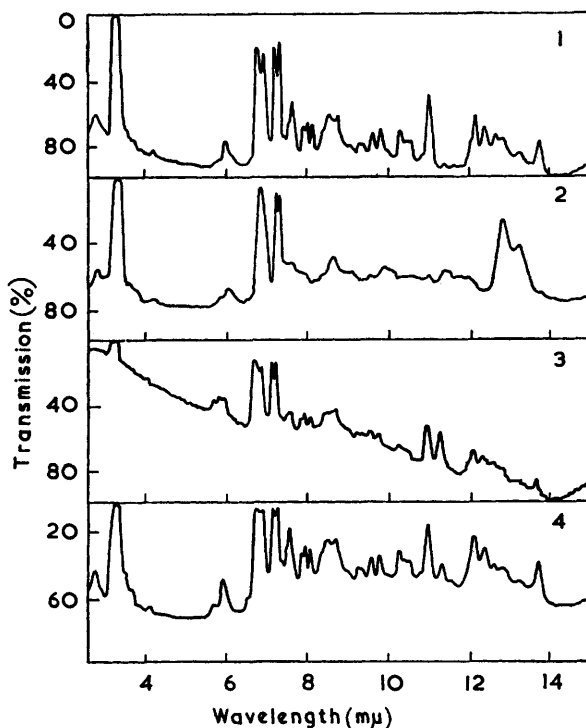
supports the vinyl group assignment. Both bromination and hydrogenation of the polymer resulted in the formation of broad, strong absorption bands in the 8—10 and the 13 μ region. The proton magnetic resonance spectrum of a saturated solution (5%) of the polymer in carbon tetrachloride gave peaks which could be ascribed to aliphatic methylene groups, allylic methylene, or methyl groups as in the structure $CMe_2:CH-$, and olefinic groups. A determination by iodination [13] gave 1·4 double bonds per monomeric unit incorporated in the polymer.

Mechanism.—The main reaction occurring on irradiation of the dry monomer *in vacuo* is polymerization, which ensues with high yield and the formation of a relatively low-molecular-weight polymer. Since the number-average degree of polymerization for the chloroform-soluble polymer is only about 10 monomer units, whereas the yield is 850 monomer molecules converted per 100 ev, it follows that the polymerization chain must be sustained by a process of chain transfer to monomer; the alternative interpretation
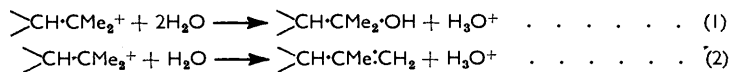
[14] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London, 1958, p. 34.

in terms of the formation of a large number (*ca.* 100) of primary initiators is discounted because such high values for primary ion- and radical-pair yields are extremely improbable from energetic considerations. Both ion and radical transfers to monomer are feasible, but the latter would probably afford an allylic radical by hydrogen-atom abstraction from the α-position to the double bond;[15] a corollary of this radical mechanism of chain transfer would be the incorporation of a terminal vinylidene group in the growing polymer after transfer. Since the vinylidene group is absent from the polymer produced under dry conditions, it is unlikely that radical transfer is applicable. Besides, an allylic radical is generally too unreactive to initiate a polymerization chain but terminates by dimerization; thus radical-chain transfer in this instance would be degradative, resulting in a suppression of chain growth. Unequivocal evidence in favour of an ionic mechanism is the strong retardation of polymerization by added water; a qualitatively similar effect was observed in the radiation-induced polymerization of α-methylstyrene[12] and has been ascribed mainly to interaction of a water molecule with the positive ion-electron pair before the propagating species can be stabilized. There is also the added possibility that water terminates an ion-propagation chain even if the initiator is formed. Regardless of the precise role of water, its action as a polymerization retarder cannot be reconciled with a radical mechanism on energetic grounds.[16] The above arguments are reinforced by the fact that β-pinene belongs to a class of monomers which are readily susceptible to cationic polymerization,[5] whereas free-radical-initiated polymerization of β-pinene has not been reported.

Ionic polymerization in a medium of low dielectric constant requires coexistence of the propagating ion with its oppositely charged species in close proximity.[17] For initiation by ionizing radiation, positive ions are formed directly but these are odd-electron species and their lifetime in the liquid state, estimated[18] at about 10^{-12} sec., is probably much too short to initiate a polymerization chain which may extend for a time of 10^{-3} sec.[19] Apart from the neutralization of the parent ion by the conjugate electron to produce an excited molecule or free radicals, other possibilities can be envisaged in this system. By analogy with α-pinene,[8,11] the parent ion may rapidly rearrange to the open structure (V) and be followed by electron capture at the radical site to give the internal ion-pair (VI). On this postulate, charge separation is achieved and polymerization then proceeds from one of
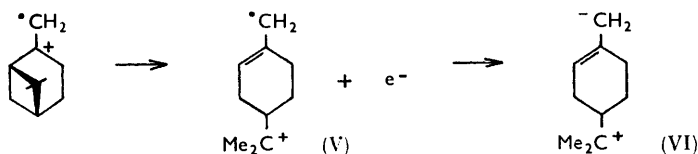
the charged centres within the lifetime of (VI) before self-termination by charge neutralization or the more likely proton transfer; for β-pinene we infer that the cationic centre is the active polymerization initiator. As a result of the first proton chain transfer, a separated negative counter-ion is formed. The effect of water on the polymerization has been assigned to a reaction with the propagating ion or its precursor; two known reactions of a carbonium ion with water in solvated systems can be represented as:

$$>CH \cdot CMe_2{}^+ + 2H_2O \longrightarrow >CH \cdot CMe_2 \cdot OH + H_3O^+ \quad \cdots \cdots \quad (1)$$

$$>CH \cdot CMe_2{}^+ + H_2O \longrightarrow >CH \cdot CMe:CH_2 + H_3O^+ \quad \cdots \cdots \quad (2)$$

[15] Cf. Walling, " Free Radicals in Solution," J. Wiley and Sons, Inc., New York, 1957, p. 175.
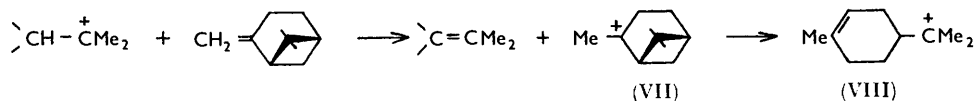[16] Bates, Best, and Williams, *Nature*, 1960, **188**, 469.
[17] Cf. Ingold, *Proc. Chem. Soc.*, 1957, 279.
[18] Burton, Hamill, and Magee, Proc. Second U.N. Conference on Peaceful Uses of Atomic Energy, Geneva, 1958, Vol. XXIX, p. 391.
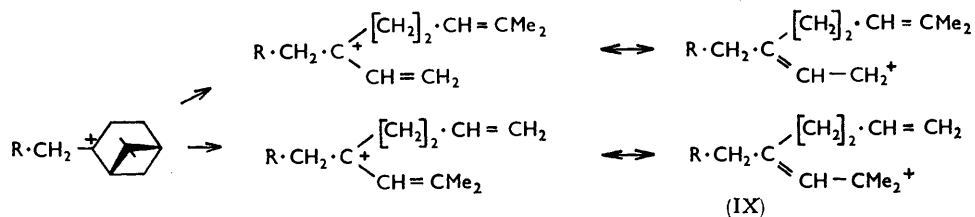[19] Collinson, Dainton, and Gillis, *J. Phys. Chem.*, 1959, **63**, 909.

The solvated proton is then likely to be involved in proton transfer to the counter-ion. Evidence in favour of the latter reaction is that the water appears to be progressively used up during the induction dose until the rate attains a maximum value. A possible reason why the maximum rate in the presence of added water, corresponding to G_f, is less than that obtained in dry systems may be connected with secondary inhibition from the alcohol formed. The identification of vinylidene groups only in the polymers formed from water-saturated runs suggests that the second reaction may also be important. If the above interpretation is correct, $G(-H_2O)$ in Table 5 represents the yield of propagating cationic centres removed by reaction (1); since the total yield of ion pairs would not be expected to exceed about 4 per 100 ev, the mean $G(-H_2O)$ of 0·9 from our results can be considered reasonable. The presence of water in the system during polymerization does not appear to affect the molecular weight of the resulting polymer; this result suggests that reaction (1) occurs primarily with the initiator before propagation can ensue. As chain transfer to monomer is an important feature of the kinetics for the dry reaction, the cation is assumed to participate in proton transfers [20] of the type represented below; proton transfer from methyl groups adjacent to a cationic centre is excluded because of the absence of vinylidene groups in the polymers formed under dry conditions. A case of proton transfer to monomer

$$\rangle CH-\overset{+}{C}Me_2 \ + \ CH_2 = \langle\!\!\langle\ \rangle\!\!\rangle \ \longrightarrow \ \rangle C=CMe_2 \ + \ Me \overset{+}{-}\langle\!\!\langle\ \rangle\!\!\rangle \ \longrightarrow \ Me\langle\!\!\langle\ \rangle\!\!\rangle -\overset{+}{C}Me_2$$

$$\text{(VII)} \qquad\qquad\qquad \text{(VIII)}$$

followed by rearrangement to (VIII) and further transfer without addition polymerization could account for the formation of dipentene, although the proton transfer from (VIII) would then have to originate from the methyl group.

It remains to consider the nature of the addition step during polymerization; β-pinene represents a special case in vinyl polymerization since the intermediate can rearrange before the addition of a subsequent monomer molecule. Apart from the repeating structure (IV) which predominates in the Friedel–Crafts polymer, other possibilities can be envisaged. Since the formation of one double bond (by transfer) at the end of a polymer chain can only account for 0·1 double bond per monomer unit incorporated in the polymer, the remainder of the unsaturation must be entirely due to the rearrangement of the bicyclic structure during polymerization. Thus the number of double bonds formed per repeating unit is equal to the number of rings broken. Since the index of double bonds is 1·4 per repeating unit, it suggests that rearrangements involving the scission of both rings can occur as well as the formation of (IV). It is pertinent to consider the rearrangement of a carbonium ion similar to (VII), as shown:

$$R\cdot CH_2\cdot C\overset{+}{\underset{CH=CH_2}{\overset{[CH_2]_2\cdot CH=CMe_2}{\Big\langle}}} \quad\rightleftharpoons\quad R\cdot CH_2\cdot C\underset{CH-CH_2^+}{\overset{[CH_2]_2\cdot CH=CMe_2}{\Big\langle}}$$

$$R\cdot CH_2\overset{+}{-}\langle\!\!\langle\ \rangle\!\!\rangle \ \nearrow \quad \rightarrow$$

$$R\cdot CH_2\cdot C\overset{+}{\underset{CH=CMe_2}{\overset{[CH_2]_2\cdot CH=CH_2}{\Big\langle}}} \quad\rightleftharpoons\quad R\cdot CH_2\cdot C\underset{CH-CMe_2^+}{\overset{[CH_2]_2\cdot CH=CH_2}{\Big\langle}}$$

$$\text{(IX)}$$

The scission of the rings depicted is analogous to the conversion of the α-pinene skeleton into ocimene; [11] the transformation to (IX) corresponds to the alternative mode of rupture of the cyclobutane ring. Both reactions would be facilitated by an excess of electronic or vibrational energy in the structure.[11] The migration of the positive charge as written in the resonating structures above may conceivably assist the subsequent polymerization since the active cationic centre would be thereby removed from a position encumbered by three large surrounding groups; the situation is completely analogous to the 1 : 4 addition

[20] Pepper, *Quart. Rev.*, 1954, **8**, 88.

in polymerization of myrcene (II) by ionic reagents.[21]   Evidence in support of our scheme comes from the assignment of $-CH=CH_2$ and $\cdot CH\colon CMe_2$ groups to the infrared and proton

magnetic resonance bands of the polymer.   Finally, it is conceivable that addition may occur in some instances with retention of the bicyclic structure either in the original form (X) or after rearrangement to the camphene structure (XI).

[21] Marvel and Hwa, *J. Polymer Sci.*, 1960, **45**, 25.