596. *The Activation of Carbon–Carbon Double Bonds by Cationic Catalysts. Part VIII.*[1] *Cyclisation of* 1 : 1 : 3 : 3-*Tetraphenylbut*-1-*ene.*

By Alwyn G. Evans and D. Price.

In previous Parts the dimerisation of 1 : 1-diphenylethylene was studied with various catalysts. In all cases so far examined the linear olefinic dimer, 1 : 1 : 3 : 3-tetraphenylbut-1-ene, was formed. The formation of a cyclic non-olefinic dimer, 3-methyl-1 : 1 : 3-triphenylindane, is possible, however, under certain conditions.[2] We have now examined the formation of this indane under rigorous high-vacuum conditions; its formation is associated with a very adverse entropy term.

Experimental

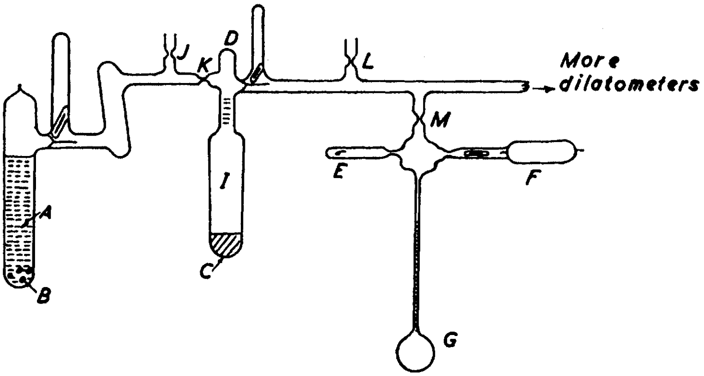
Materials.—Stannic chloride was prepared and purified as described in Part V.[3]

" AnalaR " benzene was purified by standard methods and then outgassed under high vacuum and distilled over a bright sodium film into a receiver (*A*, Fig. 1), where it was kept over sodium–potassium alloy, (*B*). Immediately before use the pure benzene was distilled off the alloy.

Hydrogen chloride was prepared by the action of " AnalaR " sulphuric acid on " AnalaR " ammonium chloride.[1]

1 : 1 : 3 : 3-Tetraphenylbut-1-ene (linear dimer, LD) was prepared by dissolving 200 g. of 1 : 1-diphenylethylene, freshly fractionated off potassium hydroxide, in 1500 ml. of " AnalaR " benzene which had been dried over sodium wire. To this solution were added 25 ml. of anhydrous B.D.H. stannic chloride. The solution was then kept in a stoppered " Quickfit " flask for 7 days. It was then washed with water to remove all trace of catalyst, and the benzene pumped off to leave the crude 1 : 1 : 3 : 3-tetraphenylbut-1-ene. This was then recrystallised 4 or 5 times from absolute ethanol to give the pure product, m. p. 113° (lit.,[2] m. p. 113°).

Fig. 1.



3-Methyl-1 : 1 : 3-triphenylindane (cyclic dimer, CD), prepared according to Schoepfle and Ryan's method,[2] had m. p. 143° (lit.,[2] m. p. 143°).

Procedure.—Dilatometers were filled with known concentrations by means of the apparatus shown in Fig. 1. The calibrated vessel (*I*) was first baked out under high vacuum and then opened at the point *D* to allow the introduction of a known weight of 1 : 1 : 3 : 3-tetraphenylbut-1-ene (*C*). The apparatus was resealed at *D* and re-evacuated. This linear dimer was then degassed by alternately melting and solidifying it under high vacuum, and the apparatus was then sealed off at *J*. The vessel (*A*) containing the purified benzene was then opened to the system by operating the magnetic breaker, and the benzene distilled on the dimer (*C*) until the vessel was filled to the calibration scale. The vessel was then sealed off at the constriction

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[1] Part VII, Evans and Lewis, *J.*, 1959, 1946.
[2] Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021.
[3] Evans and Lewis, *J.*, 1957, 2975.

K; the dimer dissolved in the benzene and the solution became homogeneous. The volume was then measured on the scale at a known temperature.

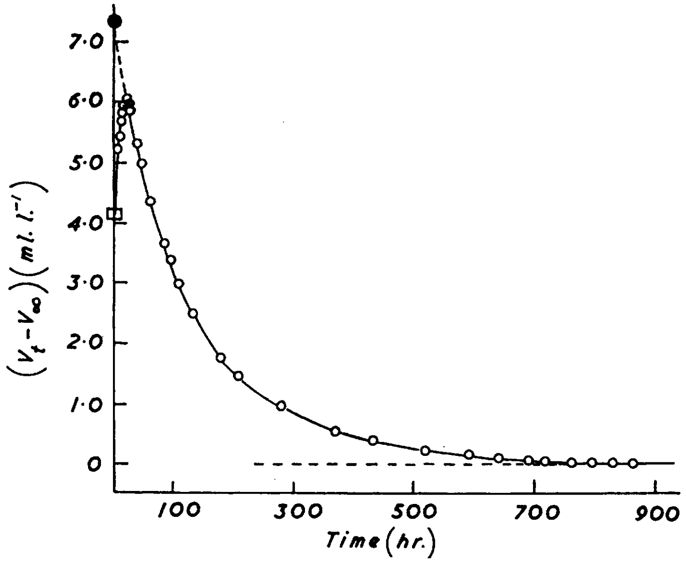
The vessel, *I*, was then sealed to the dilatometer system as shown. The whole apparatus was thoroughly evacuated and then sealed off at *L*. The linear dimer solution was then opened to the system by operating the magnetic breaker and each dilatometer was filled to a convenient point under vacuum. The dilatometer was then sealed off at *M*. Stannic chloride was introduced into the dilatometer by carefully exploding by heat the calibrated bulb in *E*, filled under high vacuum with a known volume of stannic chloride. The bulb *F* containing hydrogen chloride was then opened by operating the magnetic breaker and the gas frozen into the dilatometer bulb by use of liquid air. The dilatometer was then sealed off at the top of its stem while its bulb was still immersed in liquid air. The contents of the dilatometer were then allowed to melt and become homogeneous before the dilatometer was placed in a thermostat. The volume changes were followed in thermostats kept at 30·0°, 40·1°, and 54·9°.

The volume change involved in the conversion of 1 mole of the monomer into $\frac{1}{2}$ mole of the cyclic dimer was found to be 17·2 ml. by determining the densities of solutions containing equal weights of the monomer or cyclic dimer in the same weights of benzene at the three temperatures. The volume changes from monomer to linear dimer have been determined previously.[3] The change from linear dimer to monomer involves an expansion, and that from linear dimer to cyclic dimer a contraction.

Two dilatometers, one containing linear dimer, stannic chloride, and benzene, but no hydrogen chloride, and the other cyclic dimer, stannic chloride, hydrogen chloride, and benzene, were used as blanks.

The product of the reaction (m. p. 143°) was extracted, and found to be the indane.

Fig. 2. *Volume change during reaction at* 54·9°.



[SnCl$_4$] = 4·99 × 10^{-2} mole l.$^{-1}$, [HCl] = 1·03 × 10^{-1} mole l.$^{-1}$, [Total CD] formed at t_∞ = 4·603 × 10^{-1} mole l.$^{-1}$.

☐ Calculated initial point in terms of linear dimer.

● Calculated initial point in terms of monomer–linear dimer equilibrium mixture.

RESULTS

In order to obtain the cyclic dimer at a measurable rate much higher concentrations of stannic chloride and hydrogen chloride are required than those used for the monomer–linear dimer equilibration experiments.[1] Under these conditions of high catalyst concentration the monomer–linear dimer equilibrium is established very rapidly, and one measures the rate of production of the cyclic dimer from this equilibrium mixture of monomer and linear dimer. We therefore studied the reaction by starting with the linear dimer, and not with monomer as in the previous Parts, since in this way we can observe the rapid establishment of the monomer–linear dimer equilibrium as an expansion, and the slower formation of cyclic dimer as a contraction. This is seen in the typical reaction plot in Fig. 2, where the initial expansion is over very quickly and the subsequent contraction occurs slowly, We have included on this curve two initial points, one calculated in terms of linear dimer, and the other in terms of monomer–linear dimer equilibrium mixture, this equilibrium being assumed to be established instantaneously. The broken portion of the curve shows how the volume change would have occurred if monomer–linear dimer equilibration had occurred immediately at zero time.

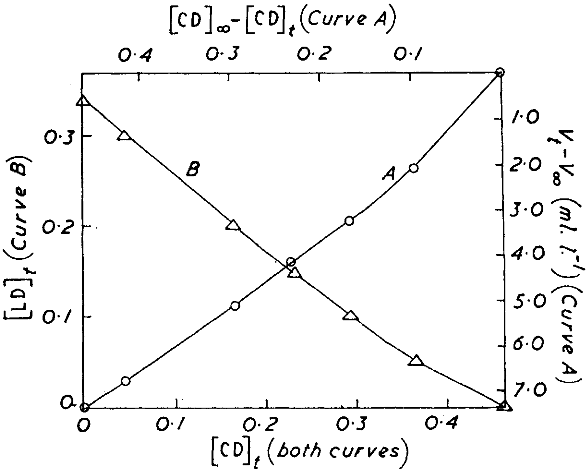


FIG. 3. *Calibration curves at* 54·9°.
[Total CD] formed at t_∞ = 4·603 × 10^{-1} mole l.$^{-1}$.

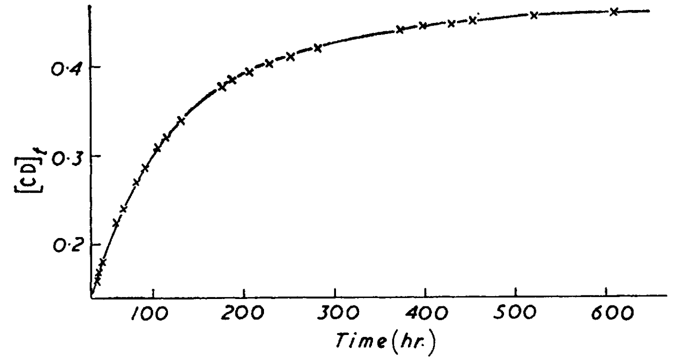


FIG. 4. *Change in* [CD] *during reaction at* 54·9°.
[$SnCl_4$] = 4·99 × 10^{-2} mole l.$^{-1}$, [HCl] = 1·03 × 10^{-1} mole l.$^{-1}$, [Total CD] formed at t = 4·603 × 10^{-1} mole l.$^{-1}$.

The dilatometer containing linear dimer, stannic chloride, and benzene but no hydrogen chloride showed no change in volume with time and was colourless. This establishes the purity of the reagents and shows that the formation of cyclic dimer requires a cocatalyst. (In earlier papers [4] we found it difficult to purify the linear dimer when it was made from the monomer by catalysis with sulphuric acid. The present method of preparation gave very pure material.)

The dilatometer containing cyclic dimer, stannic chloride, benzene, and hydrogen chloride also showed no volume change with time and was colourless. This means that, unlike the formation of the monomer from the linear dimer, the formation of cyclic dimer is irreversible. Thus the asymptote to the curve in Fig. 2 represents total conversion into cyclic dimer. If the volume at any time t is V_t and that at infinite time is V_∞, a calibration curve for converting the quantity ($V_t - V_\infty$) into the concentration of cyclic dimer still to be formed at time t is shown in Fig. 3, curve *A*. This curve also gives the relation between ($V_t - V_\infty$) and the concentration of cyclic dimer at time t. A further calibration curve has been drawn relating

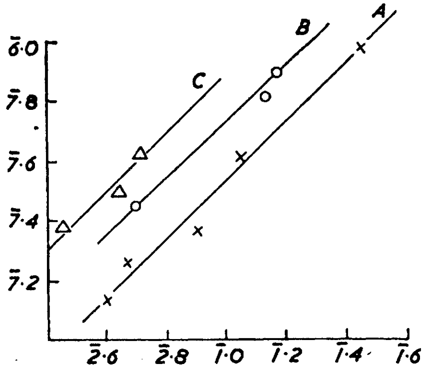
[4] (*a*) Evans, Jones, and Thomas, *J.*, 1955, 1824; (*b*) Evans, Jones, Jones, and Thomas, 1956, 2757.

the concentration of cyclic dimer at time *t* to the equilibrium concentration of linear dimer at time *t* (Fig. 3, curve *B*). All these curves are calculated from the volume changes for the complete conversion of one species into another and from the known equilibrium constants for the monomer–linear dimer equilibria.[1]

Using the calibration curve (Fig. 3, curve *A*), we have replotted that part of Fig. 2 to the right of the maximum as cyclic dimer concentration against time (Fig. 4) for all reactions. Tangents to this curve give values for the rate of formation of the cyclic dimer at this time (*t*) (since this reaction to cyclic dimer is irreversible it is not necessary, as in the monomer–linear dimer equilibration, to measure initial rates). The linear dimer concentration at time *t* is also known from the calibration curve (Fig. 3, curve *B*).

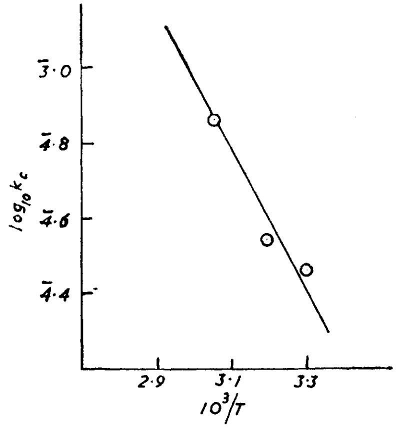
The order of reaction in linear dimer was found from the dependence of rate on [LD], (*a*) as a given reaction proceeds, and (*b*) from one reaction system to another, to be 1·0 ± 0·1 (Fig. 5).

FIG. 5. *Plots of* $\log_{10}$ (*Rate of formation of* CD) *at* 54·9° (*vertical axis*) *against* $\log_{10}$ [LD] *for curve A*, $\log_{10}$ [HCl] *for curve B*, log [$SnCl_4$] *for curve C.*



Curve *A* [HCl] = 1·028 × 10^{-1} mole l.$^{-1}$, [$SnCl_4$] = 5·146 × 10^{-2} mole l.$^{-1}$.
Curve *B* [LD] = 1·774 × 10^{-1} mole l.$^{-1}$, [$SnCl_4$] = 3·565 × 10^{-2} mole l.$^{-1}$.
Curve *C* [LD] = 1·07 × 10^{-1} mole l.$^{-1}$, [HCl] = 1·039 × 10^{-1} mole l.$^{-1}$.

FIG. 6. *Temperature dependence of* k_c.



The orders of reaction in $SnCl_4$ and HCl have been found to be 1·0 ± 0·1 in each case: there is no optimum [HCl]/[$SnCl_4$] ratio (in agreement with the findings of Part VII [1]) (see Fig. 5). Thus:

$$\text{Rate of formation of cyclic dimer} = k_c\,[\text{LD}][\text{SnCl}_4][\text{HCl}]$$

The activation energy, *E*, for cyclic dimer formation was found to be 8·7 kcal. mole^{-1} by plotting $\log_{10}k_c$ against $1/T$ (Fig. 6).

A check on the extent of the reaction was carried out by taking a known volume of the reacting solution at t_∞ and dissolving it in 98% sulphuric acid. The spectrum of this solution was measured. Since the cyclic dimer gives no colour on dissolving in this acid and any residual linear dimer is converted into monomer ion in it, the extent of the reaction can be found from the extinction coefficient of the monomer ion ($\varepsilon_{430} = 2·8 \times 10^4$). It was found

TABLE 1. *Conversion of linear dimer into cyclic dimer in the stannic chloride–hydrogen chloride–benzene system.*

k_c (sec.$^{-1}$ mole^{-2} l.^{2})	T	$\Delta H_c^\ddagger = (E - RT)$ (kcal. mole^{-1})	$\Delta G_c^\ddagger$ (30·0°) (kcal. mole^{-1})	$\Delta S_c^\ddagger$ (30·0°) (cal. mole^{-1} deg.$^{-1}$)
2·84 × 10^{-4}	30·0°	8·1	22·7	−48·1
3·47 × 10^{-4}	40·1			
7·34 × 10^{-4}	54·9			

$k_c = k_4k_{3b}/k_{3a} = k_4/K_3$; $\Delta H_c^\ddagger = \Delta H_{3b}^\circ + \Delta H_4^\ddagger$; $\Delta G_c^\ddagger = \Delta G_{3b}^\circ + \Delta G_4^\ddagger$; $\Delta S_c^\ddagger = \Delta S_{3b}^\circ + \Delta S_4^\ddagger$.

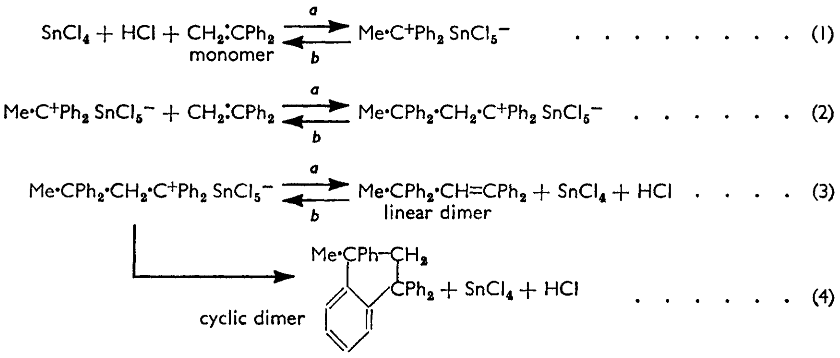
that when no further volume change with time was measurable, the original linear dimer had been completely converted into cyclic dimer to within 0·5%. Thus the formation of cyclic dimer is irreversible, and it does not give any carbonium ions in solution. Thus, as the reaction proceeds the colour of the solution (which becomes intense on adding the hydrogen chloride to the colourless linear dimer–stannic chloride–benzene [1]) gradually fades until it has almost disappeared when no further volume change with time is measurable.

The results are given in Table 1, together with the values of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$.

DISCUSSION

In our previous work we always noted that although two dimers of 1 : 1-diphenylethylene exist, only 1 : 1 : 3 : 3-tetraphenylbut-1-ene was obtained under our conditions. We have now found that the reaction to the cyclic dimer does occur at a measurable rate if the concentration of stannic chloride–hydrogen chloride catalyst is sufficiently great. At concentrations of catalyst which give this measurable rate of formation of cyclic dimer from linear dimer (velocity constant = $2{\cdot}84 \times 10^{-4}$ sec.$^{-1}$ mole^{-2} l.^{2} at 30·3°, see Table 1), the conversion of monomer into linear dimer occurs extremely rapidly (velocity constant = $2{\cdot}3 \times 10^{-2}$ mole^{-3} l.^{3} sec.$^{-1}$ at 30·0° [1]). This is why we found no cyclic dimer earlier [1] when the stannic chloride–hydrogen chloride catalyst concentration was that necessary to give a measurable rate for the formation of linear dimer from monomer.

We interpret our results, taken together with those of Part VII,[1] as follows:



Reactions (1), (2), and (3) are reversible and are discussed in Part VII. The reaction of the 1 : 1 : 3 : 3-tetraphenylbut-1-ene to the indane will go through the 1 : 1 : 3 : 3-tetraphenylbut-1-ene ion, and thus the change will involve reaction (3*b*), followed by irreversible reaction (4).

In the present work we started with the linear dimer. The rate-determining step for the production of monomer from the linear dimer is reaction (2*b*).[4a] In our previous work the catalyst concentration was low, and we followed the conversion of monomer into linear dimer. At high catalyst concentrations, the equilibria (3), (2), and (1) are established rapidly, and it is reaction (4) which becomes the measured rate-determining step.

Thus:

Rate of formation of CD

$$= k_4[\mathrm{LDH^+SnCl_5^-}] = (k_4/K_3)[\mathrm{LD}][\mathrm{SnCl_4}][\mathrm{HCl}] = (k_4k_{3b}/k_{3a})[\mathrm{LD}][\mathrm{SnCl_4}][\mathrm{HCl}]$$

This agrees with the relationship we find experimentally:

$$\text{Rate of formation of CD} = k_c[\mathrm{LD}][\mathrm{SnCl_4}][\mathrm{HCl}]$$

and therefore $k_c = k_4/K_3 = k_4k_{3b}/k_{3a}$. Data are given in Tables 1 and 2 and the reaction process is shown diagrammatically in Fig. 7. This diagram shows the reaction of a monomer molecule with another monomer molecule to form a linear dimer, and then the further

TABLE 2. *Conversion of linear dimer into monomer in the stannic chloride–hydrogen chloride–benzene system.**

k_r (sec.$^{-1}$ mole^{-2} l.^{2})	T	$\Delta H_r^\ddagger = (E - RT)$ (kcal. mole^{-1})	$\Delta G_r^\ddagger$ (30·3°) (kcal. mole^{-1})	$\Delta S_r^\ddagger$ (30·3°) (cal. mole^{-1} deg.$^{-1}$)
$1{\cdot}14 \times 10^{-3}$	30·3°	14·4	21·9	−24·8
$2{\cdot}54 \times 10^{-3}$	39·9			
$7{\cdot}82 \times 10^{-3}$	55·0			

* These values are obtained from the results given in Part VII [1] for the conversion of monomer into linear dimer.

$k_r = k_{2b}k_{3b}/k_{3a} = k_{2b}/K_3$; $\Delta H_r^\ddagger = \Delta H_{3b}^\circ + \Delta H_{2b}^\ddagger$; $\Delta G_r^\ddagger = \Delta G_{3b}^\circ + \Delta G_{2b}^\ddagger$; $\Delta S_r^\ddagger = \Delta S_{3b}^\circ + \Delta S_{2b}^\ddagger$.

reaction of the linear dimer, not with another monomer to form a trimer, but with a double bond within its own molecule to form a cyclic dimer.

The process *A* to *B* involves the bringing together of HCl, $SnCl_4$ and two monomer molecules, and so has a very negative entropy change.

The process *D* to *E* involves HCl, $SnCl_4$, and only one olefin molecule, but since it involves a very special orientation of the linear dimer ion to form the cyclic dimer, so it has a very negative entropy change (this orientation can be seen from Courtauld atomic models). The enthalpy change associated with this process is greater than that of step *A* to *B*, presumably because of the greater steric repulsion involved in the cyclisation.

The process *D* to *B* involves HCl, $SnCl_4$, and only one olefin molecule, and so has a much less negative entropy change since the very special orientation of the linear dimer ion described above is not required here. The enthalpy change for this process is large because a single bond is being broken and the second half of a double bond (which is weaker) is being formed.

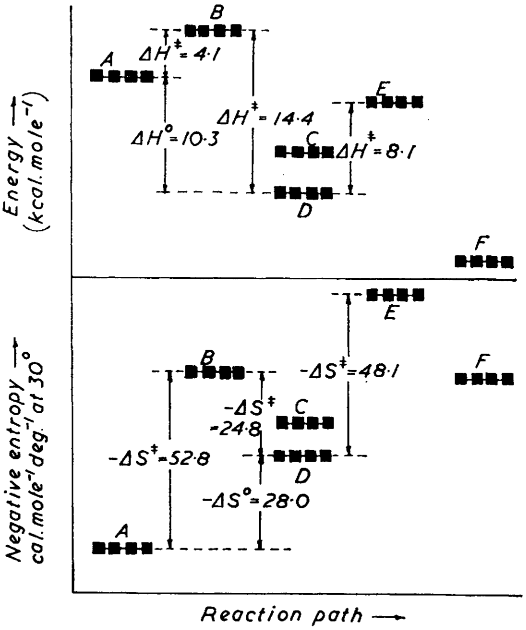


FIG. 7. *Reaction-path diagram.*

A. Initial state of reaction (1); monomer + monomer + HCl + $SnCl_4$.
B. Transition state of reaction (2).
C. Final state of reaction (2); linear dimer ion(+) $SnCl_5$(−).
D. Final state of reaction (3); linear dimer + HCl + $SnCl_4$.
E. Transition state of reaction (4).
F. Final state of reaction (4); cyclic dimer + HCl + $SnCl_4$.

The energy and entropy values are taken from the present paper and from Part VII.[1] The positions of states *C* and *F* are not quantitatively known.

The linear dimer changes into monomer at a faster rate than it changes into cyclic dimer; k_r/k_c [*i.e.*, $(k_{2b}/K_3)/(k_4/K_3) = k_{2b}/k_4$] varies from 4 at 30° to 10·5 at 55°. This is interesting since the enthalpy of activation for monomer formation is 14·4 kcal. mole^{-1}, compared with a value of 8·1 kcal. mole^{-1} for the formation of cyclic dimer. The rate of the cyclic dimer formation is slower because it is associated with a much more negative entropy of activation (—48·1 cal. mole^{-1} deg.$^{-1}$) than that obtaining for the production of monomer (—24·8 cal. mole^{-1} deg.$^{-1}$).

In the reaction scheme (1), (2), (3), and (4) we have all the steps involved in a cationic polymerisation. Reaction (1*a*) is initiation, (2*a*) is propagation, (3*a*) and (4) are alternative terminations leading to a linear unsaturated molecule or a cyclic saturated molecule. Termination by cyclisation has clearly a very adverse entropy owing to orientation requirements. Thus it will be much more probable that the linear unsaturated molecule is formed from the ion (reaction 3*a*), but since the latter reaction is reversible (3*b*) and reaction (4) is irreversible, the system must all move over to the cyclic saturated molecule in time. At low catalyst concentrations, however, this is a very slow process because equilibrium (3) lies well over to the right. At high catalyst concentrations, however, the concentration of linear dimer ion will be increased [*i.e.*, equilibrium (3) will be moved over to the left] and hence the rate of formation of cyclic saturated molecules will be increased. This means that although the probability of the ion's achieving the right configuration is small, when the number of these ions is increased sufficient find the correct arrangement to give a measurable rate of formation of the cyclic structure.

It has been shown [5] that, in the polymerisation of monomeric α-alkylstyrenes with sulphuric acid, a saturated cyclic and an unsaturated non-cyclic dimer are produced. As the concentration of the catalyst is increased more cyclic dimer is produced relative to unsaturated non-cyclic dimer. This agrees with our results. Hukki [6] also obtained saturated and unsaturated dimers from α*p*-dimethylstyrene using formic acid as dimerising agent. The polymerisation of α-methylstyrene catalysed by stannic chloride in ethyl chloride solution has been studied by Dainton and Tomlinson,[7] who also obtained both saturated and unsaturated polymers.

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[5] U.S. Patent 2,329,719, Oct. 28th, 1947.
[6] Hukki, *Acta Chem. Scand.*, 1949, 279—296.
[7] Dainton and Tomlinson, *J.*, 1953, 151.