389. *The Activation of Carbon–Carbon Double Bonds by Cationic Catalysts. Part VII.* Dimerization of* 1 : 1-*Diphenylethylene to* 1 : 1 : 3 : 3-*Tetraphenylbut*-1-*ene in the System Benzene–Stannic Chloride–Hydrogen Chloride.*

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Dimerization of 1 : 1-diphenylethylene in benzene–stannic chloride–hydrogen chloride has been studied dilatometrically. The initial rate of dimerization is of first order with respect to both stannic chloride and hydrogen chloride, no reaction occurring in the absence of either. Non-reacting systems are colourless, but reacting systems have an absorption spectrum similar to that given by this olefin dimerizing in benzene–stannic chloride–water.[1]

EARLIER Parts reported the dimerization of 1 : 1-diphenylethylene and its derivatives with use of trichloroacetic acid, iodine, and stannic chloride–water as catalysts. This work has now been extended by using stannic chloride–hydrogen chloride as catalyst.

EXPERIMENTAL

Materials.—Stannic chloride was prepared by the electrolysis of fused anhydrous stannous chloride under high-vacuum conditions (Part V [1]). Benzene and 1 : 1-diphenylethylene were purified by the rigorous methods described in Part V.[1] Hydrogen chloride was prepared by the action of "AnalaR" concentrated sulphuric acid on "AnalaR" ammonium chloride, and collected at about 700 mm. Hg pressure in a Pyrex glass apparatus which had been baked out under a high vacuum. Sections of this apparatus could be isolated by closing taps lubricated with "Apiezon" grease, and the gas was purified by condensation and evaporation from vapour traps cooled alternately by liquid nitrogen and by solid carbon dioxide–acetone, the system being pumped out each time the hydrogen chloride was solidified. The pure gas was admitted through long capillary stems to a series of glass bulbs of various known capacities. When the gas had attained the laboratory temperature, the pressure, measured by a mercury manometer, was adjusted to about 700 mm. Hg, and the bulbs were sealed off at graduation marks on the capillary stems.

Procedure.—The bulbs containing known amounts of hydrogen chloride were fused to the ends of the stems of dilatometers. The hydrogen chloride bulbs were provided with fragile, sealed capillaries which could be shattered by iron-in-glass breakers when it was required to transfer the gas to the dilatometer. The dilatometers were filled, through side tubes joined to the stems, with known amounts of 1 : 1-diphenylethylene, stannic chloride, and benzene, by use of the high-vacuum technique, method A, described in Part V.[1] The filled dilatometers were separated, each with its hydrogen chloride bulb, by sealing off at the side tubes. The connecting capillaries were shattered by impact from the breakers, and the hydrogen chloride was withdrawn into the dilatometers by immersing the dilatometer bulbs in liquid nitrogen, and the filling tubes together with the empty hydrogen chloride bulbs were removed by sealing off near the tops of the dilatometer stems. Dilatometers were filled in this way with solutions having various known concentrations in 1 : 1-diphenylethylene, stannic chloride, and hydrogen chloride. In some instances, optical cells were filled jointly with the dilatometers.

The dilatometers and optical cells were kept at 30·3°, 39·9°, and 55·0° in thermostats (±0·05°). The volume changes were followed in the dilatometers, and the rate of volume change was converted into mole $l.^{-1}$ $sec.^{-1}$ of dimer produced as described in Parts I [2]a nd II,[3] by using the following values for the volume change accompanying the complete conversion of 1 mole of monomer into $\frac{1}{2}$ mole of dimer: 11·95 ml. at 30·3°, 11·70 ml. at 39·9°, and 12·60 ml. at 55·0° (see Part V [1]). The spectra were measured in the optical cells by a Unicam S.P. 500 spectrophotometer.

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* Part VI, Evans, Jones, and Thomas, *J.*, 1958, 4563.

[1] Evans and Lewis, *J.*, 1957, 2975.

[2] Evans, Jones, and Thomas, *J.*, 1955, 1824.

[3] Evans, Jones, Jones, and Thomas, *J.*, 1956, 2757.

RESULTS

In the absence of hydrogen chloride, systems containing rigorously purified benzene, olefin, and stannic chloride reacted at a negligible rate (Fig. 1, curve *A*). On introduction of hydrogen chloride to such a system a great increase in the reaction rate was observed (Fig. 1, curve *A'*). No volume change occurred when hydrogen chloride was admitted to similar systems in the absence of stannic chloride, or when the monomer was omitted. It is evident, therefore, that hydrogen chloride is a cocatalyst for this reaction of the monomer. Systems containing benzene, olefin, stannic chloride, and hydrogen chloride were found, within the limits of the concentrations used, to give reaction curves (Fig. 1, curves *A'*, *B*, and *C*) similar to those obtained in the water-cocatalysed reaction (Part V), the volume decreasing until a constant value was obtained. As in the previous work, the product of the reaction, separated as described in Part I,[2] was found to be solely 1 : 1 : 3 : 3-tetraphenylbut-1-ene (cf. Schoepfle and Ryan [4]); agreement between the amount of dimer obtained from the equilibrium solutions and that expected from the observed volume change was again within the limits ±5%. Initial rates of reaction were found from the initial slopes of the reaction curves, and the dependence of rate on concentration of hydrogen chloride, for a set of fixed concentrations of stannic chloride and constant initial olefin concentration, is shown in Table 1. Initial rates of dimerization in absence of hydrogen chloride are negligible, and the initial rates vary linearly with hydrogen chloride concentration over the considerable range for which these rates have been determined. There is no optimum [HCl]/[$SnCl_4$] ratio as was found for the [H_2O]/[$SnCl_4$] ratio.[1] Using the results of Table 1 we have plotted log (initial rate) against log [initial monomer] for constant [stannic chloride]

FIG. 1. *Volume change during reaction at* 39·9°.

Curve *A* [Initial monomer] 1·33 mole $l.^{-1}$. [Stannic chloride] 4·90 × 10^{-2} mole $l.^{-1}$.

Curve *A'* As *A* with hydrogen chloride (5·12 × 10^{-2} mole $l.^{-1}$) added.

Curve *B* [Initial monomer] 0·84 mole $l.^{-1}$. [Stannic chloride] 5·49 × 10^{-3} mole $l.^{-1}$. [Hydrogen chloride] 4·00 × 10^{-2} mole $l.^{-1}$.

Curve *C* [Initial monomer] 1·40 mole $l.^{-1}$. [Stannic chloride] and [hydrogen chloride] as *B*.

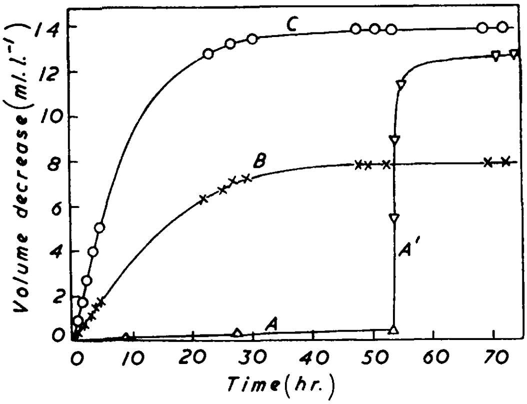

TABLE 1. *Variation in initial rate at* 39·9° *with monomer, stannic chloride, and hydrogen chloride concentrations.*

[Initial monomer] (mole $l.^{-1}$)	[Stannic chloride] (10^{-3} mole $l.^{-1}$)	[Hydrogen chloride] (10^{-3} mole $l.^{-1}$)	Initial rate of dimer formation (10^{-3} mole $l.^{-1}$ $hr.^{-1}$)	[Initial monomer] (mole $l.^{-1}$)	[Stannic] chloride] (10^{-3} mole $l.^{-1}$)	[Hydrogen chloride] (10^{-3} mole $l.^{-1}$)	Initial rate of dimer formation (10^{-3} mole $l.^{-1}$ $hr.^{-1}$)
1·33	11·2	Nil	1·9	1·33	2·35	Nil	0·3
1·33	11·2	8·40	17·1	1·33	2·35	3·85	2·14
1·33	11·2	12·5	27·4	1·33	2·35	7·99	2·99
1·33	11·2	23·5	48·7	1·33	2·35	10·2	4·92
1·33	5·49	Nil	0·5	0·85	14·9	57·2	68·4
1·33	5·49	5·72	5·69	1·40	14·9	57·2	169·0
1·33	5·49	10·4	9·40	1·96	14·9	57·2	363·0
1·33	5·49	27·1	29·9				
1·33	5·49	40·5	41·9	1·33	2·35	10·0	4·52
				1·33	5·49	10·0	10·7
				1·33	11·2	10·0	21·1

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[4] Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021.

and constant [hydrogen chloride]; log (initial rate) against log [stannic chloride] for constant [initial monomer] and constant [hydrogen chloride]; and log (initial rate) against log [hydrogen chloride] for constant [initial monomer] and constant [stannic chloride]. We find the orders in monomer, stannic chloride, and hydrogen chloride to be, respectively: 2·0 ± 0·3, 1·0 ± 0·1, and 1·0 ± 0·2.

The concentrations of monomer and dimer at equilibrium, $[M]_e$ and $[D]_e$, have been obtained for solutions of different monomer concentrations as described in Part I [2] (see Table 2). If we plot log $[D]_e$ against log $[M]_e$, we obtain a straight line of slope 2·2 ± 0·2, showing that $[D]_e/[M]_e^2 = K$. The equilibrium constants, K, are independent of the concentrations of stannic chloride and of hydrogen chloride (see Table 3). Mean values of K are given for the three temperatures in Table 4, and the plot of log K against $1/T$ has been used to find the exothermicity of the reaction: the value obtained ($-\Delta H°$) from the slope of this line is 10·3 ± 0·5 kcal. mole^{-1} (see Table 4). The values of $\Delta G°$ and $\Delta S°$ for this dimerization are also given in Table 4.

FIG. 2(*a*) *Spectrum of system given in Fig.* 1, *curve A.*

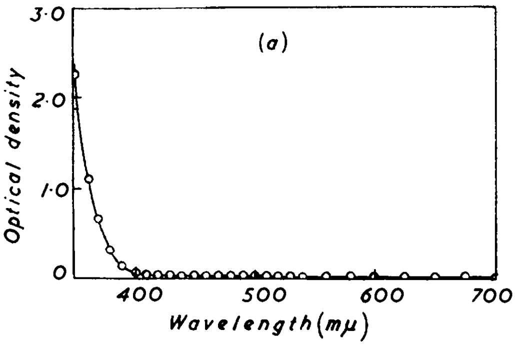
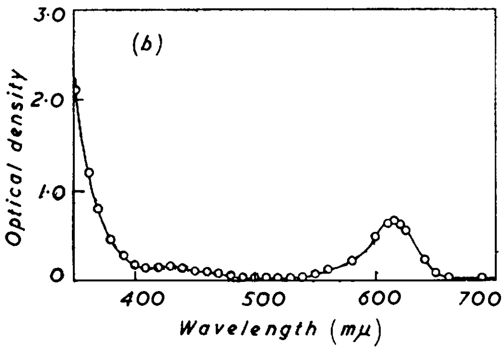


FIG. 2(*b*) *Spectrum of system given in Fig.* 1, *curve A′.*



As in our study of the water-cocatalysed reaction (Part V [1]), we have examined the spectra of the solutions in the absence and in the presence of the cocatalyst, and again we find that

TABLE 2. $[M]_e$ *and* $[D]_e$ *at* 39·9°.

$[M]_e$ (M)	$[D]_e$ (M)	Slope of log $[D]_e$–log $[M]_e$ plot
0·170	0·339	
0·220	0·589	2·2 ± 0·2
0·260	0·856	

TABLE 3.

Temp.	[Initial monomer] (mole l.$^{-1}$)	[Stannic chloride] (10^{-3} mole l.$^{-1}$)	[Hydrogen chloride] (10^{-3} mole l.$^{-1}$)	K (mole^{-1} l.)
39·9°	1·33	11·2	8·4	11·9
39·9	1·33	11·2	23·5	12·4
39·9	1·33	5·49	10·4	12·3 (Mean 12·2)

TABLE 4. *Dimerisation of* 1 : 1-*diphenylethylene to* 1 : 1 : 3 : 3-*tetraphenylbut*-1-*ene in stannic chloride–hydrogen chloride–benzene.*

k_f* (mole^{-3} l.^{3} sec.$^{-1}$)	E_f (kcal. mole^{-1})	K (mole^{-1} l.)
2·3 × 10^{-2} (30·3°)	4·7 ± 0·5	20·1 ± 0·5 (30·3°)
3·1 × 10^{-2} (39·9°)		12·2 ± 0·5 (39·9°)
4·3 × 10^{-2} (55·0°)		5·5 ± 0·2 (55·0°)

* k_f is expressed in terms of the number of moles per l. of dimer appearing per second.

$\Delta G_f‡$ (kcal. mole^{-1})	$\Delta H_f‡ = (E_f - RT)$ (kcal. mole^{-1})	$\Delta S_f‡$ (cal. deg.$^{-1}$ mole^{-1})	$\Delta G°$ (kcal. mole^{-1})	$\Delta H°$ (kcal. mole^{-1})	$\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})
20·1 (30·3°)	4·1	−52·8 (30·3°)	−1·8 (30·3°)	−10·3	−28·0 (30·3°)

addition of the cocatalyst to the colourless solutions of monomer and stannic chloride in benzene not only brings about reaction but is marked by a change in the spectrum to give absorption in the violet end of the visible region and a peak in the 600 mμ region (see Fig. 2*b*).

Activation Energy for the Stannic Chloride–Water System.—The results given in Part V for the stannic chloride–water system have now been extended to include the rate constants for this reaction at 30·3°, 39·9°, and 55·0°. The values are given in Table 5 and the activation energy E_f obtained from these is 7·9 kcal. mole^{-1}.

TABLE 5. *Dimerisation of* 1 : 1-*diphenylethylene to* 1 : 1 : 3 : 3-*tetraphenylbut*-1-*ene in stannic chloride–water–benzene.*

k_f * (mole^{-3} l.^{3} sec.$^{-1}$)	E_f (kcal. mole^{-1})	K (mole^{-1} l.)
6·8 × 10^{-3} (30·3°)	7·9 ± 0·2	19·9 ± 0·4 (30·3°)
9·9 × 10^{-3} (39·9°)		11·2 ± 0·4 (39·9°)
18·2 × 10^{-3} (55·0°)		5·4 ± 0·2 (55·0°)

* k_f is expressed in terms of the number of moles per l. of dimer appearing per second.

$\Delta G_f^‡$ (kcal. mole^{-1})	$\Delta H_f^‡ =$ $(E_f - \mathbf{R}T)$ (kcal. mole^{-1})	$\Delta S_f^‡$ (cal. deg.$^{-1}$ mole^{-1})	$\Delta G°$ (kcal. mole^{-1})	$\Delta H°$ (kcal. mole^{-1})	$\Delta S°$ (cal. deg.$^{-1}$ mole^{-1})
20·7 (30·3°	7·3	−44·2 (30·3°)	−1·8 (30·3°)	−10·5	−28·7 (30·3°)

The values of K, $\Delta G°$, $\Delta H°$, and $\Delta S°$ are taken from Part V.

DISCUSSION

1 : 1-Diphenylethylene is not dimerized by stannic chloride in benzene unless a cocatalyst is present. This was shown in Part V, where water as co-catalyst was studied. The present work shows that hydrogen chloride is also a co-catalyst in this reaction, although, in the absence of stannic chloride, it does not polymerize or react with the monomer.

Any mechanism for the dimerization of 1 : 1-diphenylethylene in benzene–stannic chloride–hydrogen chloride systems must account for the following observations. The initial rate of dimerization is of (*a*) second order in monomer, (*b*) first order in stannic chloride, (*c*) first order in hydrogen chloride; also (*d*) the order in catalyst is the same in the forward and the reverse direction (since $[D]_e/[M]_e^2 = K$, independent of the catalyst concentration).

We postulate the following mechanism where M = monomer, and D = dimer:

$$\mathrm{M + SnCl_4 + HCl \underset{b}{\overset{a}{\rightleftharpoons}} HM^+(SnCl_5)^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{M + HM^+(SnCl_5)^- \underset{b}{\overset{a}{\rightleftharpoons}} HD^+(SnCl_5)^-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{HD^+(SnCl_5)^- \underset{b}{\overset{a}{\rightleftharpoons}} D + SnCl_4 + HCl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This mechanism will account for the results if we make the same assumption as in Part V that reaction (2*a*) is the rate-controlling step. Then the initial rate of dimerization, as observed experimentally, is given by:

$$\begin{aligned}\text{Initial rate} &= k_{2a}[\mathrm{HM^+(SnCl_5)^-}][\mathrm{M}]\\ &= k_{2a}(k_{1a}/k_{1b})[\mathrm{SnCl_4}][\mathrm{HCl}][\mathrm{M}]^2\end{aligned}$$

This expression is consistent with our results, and the velocity constant, k_f, for the dimerization has been evaluated from the expression:

$$\text{Initial rate} = k_f[\mathrm{SnCl_4}][\mathrm{HCl}][\mathrm{M}]^2$$

$$\text{where } k_f = k_{2a} \,.\, k_{1a}/k_{1b} = k_{2a}K_1$$

This constant is given for each temperature in Table 4. From these values of k_f, the corresponding activation energy, E_f, was calculated and found to be 4·7 kcal. mole^{-1}. The values of K, ΔG°, ΔH°, and ΔS° obtained for this dimerization (see Table 4) are in good agreement with those obtained in our previous work on the dimerization of 1 : 1-diphenylethylene with trichloroacetic acid in benzene [2] and in nitroethane; [3] with iodine in β-nitropropane; [5] and with stannic chloride–water in benzene.[1]

The stannic chloride–hydrogen chloride catalysed reaction differs from the stannic chloride–water catalysed reaction in the following ways: (*a*) The velocity constant of the HCl-cocatalysed reaction is greater than that of the H_2O-cocatalysed reaction. The activation energy for the dimerization is reduced from 7·9 kcal. mole^{-1} to 4·7 kcal. mole^{-1} on changing from water to hydrogen chloride. The effect of this decrease of 3·2 kcal. mole^{-1} on the rate of reaction is partly offset by an accompanying decrease in the entropy of activation (see Tables 4 and 5).

(*b*) There is no optimum $[HCl]/[SnCl_4]$ ratio as there is for the $[H_2O]/[SnCl_4]$ ratio. This means that no stable stannic chloride–hydrogen chloride complex is formed. Either the proton transfer occurs in a 3-body reaction as given in equation (1), or, which is practically the same, an equilibrium may exist of the type:

$$SnCl_4 + HCl \underset{b}{\overset{a}{\rightleftharpoons}} SnCl_4,HCl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

which lies well to the left, followed by the proton transfer:

$$SnCl_4,HCl + M \underset{b}{\overset{a}{\rightleftharpoons}} MH^+SnCl_5^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

In this case:

$$\begin{aligned} \text{Initial rate} &= k_{2a}[HM^+(SnCl_5)^-][M] \\ &= k_{2a}(k_{5a}/k_{5b})[SnCl_4,HCl][M]^2 \\ &= k_{2a}(k_{5a}/k_{5b})(k_{4a}/k_{4b})[SnCl_4][HCl][M]^2 \\ \text{and } k_t &= k_{2a}(k_{5a}/k_{5b})(k_{4a}/k_{4b}) = k_{2a}K_5K_4 \end{aligned}$$

In related work on hydrogen chloride–aluminium chloride complexes, Brown and Pearsall [6] could find no evidence for the existence of the corresponding complex $HAlCl_4$, although in the presence of aromatic hydrocarbons, ternary complexes of great stability are formed which correspond in properties to salts of a very strong acid having the composition of this hypothetical complex.

(*c*) There is no evidence of solvation of the ion pairs by the catalyst, as there is when water is the cocatalyst. The fact that a stannic chloride–hydrogen chloride complex does not exist in these systems, or, if it does, is present in very small concentrations, whereas evidence for a stable $SnCl_4,2H_2O$ complex is found in the stannic chloride–water system, shows that the attraction between chlorine and $SnCl_4$ is much less than between oxygen and $SnCl_4$. It is not surprising then that although $SnCl_4$ solvates the $MH^+(SnCl_4,H_2O\,OH)^-$ ion pair, it does not solvate the $MH^+(SnCl_5)^-$ ion pair. It is also found that although $SnCl_4,2H_2O$ helps to solvate the $MH^+(SnCl_4,H_2O\,OH)^-$ ion pair there is no evidence for solvation of the $MH^+(SnCl_5)^-$ by $SnCl_4,HCl$. This is to be expected since the acid $SnCl_4,2H_2O$ will form hydrogen bonds with the $(SnCl_4,H_2O\,OH)^-$ ion, but one would not expect hydrogen bonding between $SnCl_4,HCl$ and the $SnCl_5^-$ ion.

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[5] Evans, Jones, and Thomas, *J.*, 1957, 2095.

[6] Brown and Pearsall, *J. Amer. Chem. Soc.*, 1951, **73**, 4681.