684. *The Activation of Carbon–Carbon Double Bonds by Cationic Catalysts. Part X.*[1] *The Reaction between* 1,1,3,3-*Tetraphenylbut-*1-*ene, Antimony Trichloride, and Hydrogen Chloride in Benzene.*

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The reaction of 1,1,3,3-tetraphenylbut-1-ene in the presence of antimony trichloride and hydrogen chloride in benzene has been studied by a dilatometric method. No reaction occurs in the absence of hydrogen chloride or in the absence of antimony trichloride. The initial rate of reaction is of the first order in the butene and in hydrogen chloride, and of the third order in antimony trichloride. It proceeds to the equilibrium mixture of 1,1-diphenylethylene and 1,1,3,3-tetraphenylbut-1-ene, which in the presence of large concentrations of antimony trichloride slowly gives 3-methyl-1,1,3-triphenylindane.

The reaction of 1,1-diphenylethylene in the presence of antimony trichloride and hydrogen chloride has also been studied in benzene. It is of the first order in 1,1-diphenylethylene and proceeds to the equilibrium mixture of this with the tetraphenylbutene.

In earlier parts, the action of cationic catalysts on 1,1-diphenylethylene and its linear dimer, 1,1,3,3-tetraphenylbut-1-ene, has been examined by using a dilatometric method to follow the reaction. We have now extended this work by studying the catalytic action of antimony trichloride–hydrogen chloride on these olefins.

Experimental

Materials.—" AnalaR " antimony trichloride was sublimed several times under a high vacuum, the middle fraction only being retained each time. Finally it was sublimed into calibrated ampoules fitted with magnetically operated breakers and sealed off under a high vacuum. The ampoules were then placed in a water-bath at 75° and when the antimony trichloride melted its volume was measured on the calibrated stem. The density at this temperature being known,[2] the weight was calculated. When solutions of antimony trichloride in benzene were required, it was dissolved in benzene under a high vacuum, to give a stock solution for dilution as required.

1,1,3,3-Tetraphenylbut-1-ene (linear dimer) was prepared and purified as in Part VIII.[3] Hydrogen chloride was prepared as in Part VII.[4] Benzene, purified as in Part VIII,[3] was stored for several months under a high vacuum in vessels fitted with magnetically operated breakers and containing sodium–potassium alloy.

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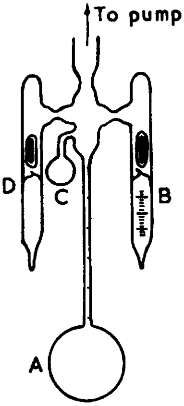
[1] Part IX, Evans and Owen, *J.*, 1959, 4123.
[2] Jager, *Z. anorg. Chem.*, 1917, **101**, 1.
[3] Evans and Price, *J.*, 1959, 2982.
[4] Evans and Lewis, *J.*, 1959, 1946.

1,1-Diphenylethylene (monomer) was prepared and purified as described in Part V.[5]

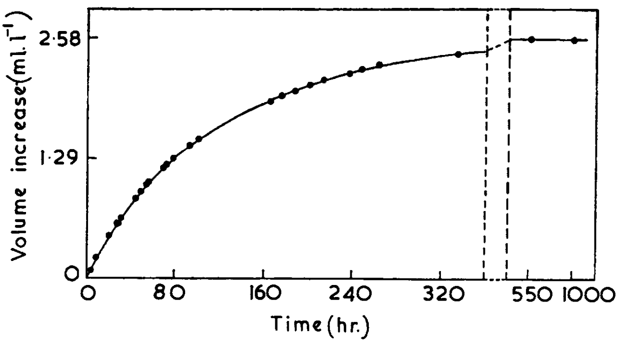
Procedure.—This was the same as described in Part VIII,[3] except that antimony trichloride was used instead of stannic chloride. The apparatus for adding the catalyst to the benzene solution of the olefin is shown in Fig. 1. When small concentrations of antimony trichloride were required, vessel B contained a benzene solution of antimony trichloride, but for high concentrations the solid was used.

FIG. 1. *Apparatus.*



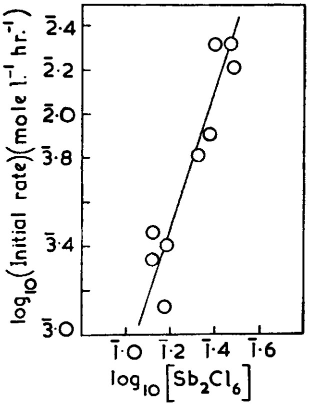
A, *Dilatometer.* B, *Catalyst ampoule.* C, *Optical cell.* D, *Cocatalyst ampoule.*

FIG. 2. *A typical reaction curve.*



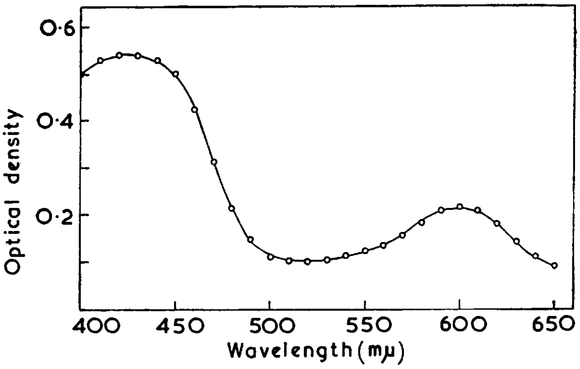
[Sb_2Cl_6] = 0·15 mole l.$^{-1}$. [HCl] = 1·55 × 10^{-2} mole l.$^{-1}$. [Linear dimer] = 0·70 mole l.$^{-1}$. Temp. = 40°.

FIG. 3. *Order in* Sb_2Cl_6 *at* 40°.



[Linear dimer] = 0·78 mole l.$^{-1}$. [HCl] = 2·0 × 10^{-2} mole l.$^{-1}$. Slope = 3.

FIG. 4. *Spectrum of solution. This solution was colourless for the first* 120 *hours after which the colour began to develop.*



[Sb_2Cl_6] = 0·31 mole l.$^{-1}$. [Linear dimer] = 0·78 mole l.$^{-1}$. [HCl] = 2·33 × 10^{-2} mole l.$^{-1}$. Temp. = 40°.

Results.—*Orders in reagents.* In the absence of hydrogen chloride, dilatometers containing rigorously purified benzene, linear dimer, and antimony trichloride showed no volume change over a period of several weeks. On the introduction of hydrogen chloride the volume increased with time and reached a stationary value (Fig. 2). The expansion observed was, within 5%, that expected for the conversion of linear dimer into the equilibrium mixture of monomer and linear dimer,[5] and hence the values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the reaction are the same as those obtained earlier for the stannic chloride–hydrogen chloride system. Initial rates of reaction were found from the initial slopes of the reaction curves, and their dependence on reagent

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

concentration is shown in Tables 1 and 2 and Fig. 3. It is seen that the order in hydrogen chloride is 1·0 ± 0·2, in linear dimer is 1·0 ± 0·1, and in antimony trichloride is 3. For systems containing high antimony trichloride concentrations, ([Sb_2Cl_6] > 0·21 mole l.$^{-1}$) the stationary period of monomer–linear dimer equilibrium was followed by a slow decrease in volume. Analysis of the solution showed that this decrease was due to the formation of the cyclic dimer, 3-methyl-1,1,3-triphenylindane.

Use of dilatometers containing the monomer, 1,1-diphenylethylene, benzene, antimony trichloride, and hydrogen chloride disclosed a volume decrease with time; when no further change occurred, the contraction was, within 5%, that expected for the conversion of monomer into the monomer–dimer equilibrium mixture.[5] The dependence of initial rate on monomer concentration is shown in Table 3, and it is seen that the order in monomer is 1·0 ± 0·1.

Temperature-dependence. The initial rate of conversion of linear dimer into monomer varies over the temperature range 30—55° as shown in Table 4. A plot of $\log_{10}$ (Initial rate/[HCl]) against $1/T$ gives a good straight line from which the activation energy is found to be 11·5 kcal. mole^{-1}.

TABLE 1. *Order in* HCl *at* 40°.

[LD] * (mole l.$^{-1}$)	[Sb_2Cl_6] (mole l.$^{-1}$)	[HCl] (10^{-2} mole l.$^{-1}$)	IR * (10^{-3} mole l.$^{-1}$ hr.$^{-1}$)	IR */[HCl] (10^{-2} hr.$^{-1}$)
0·58	0·15	1·16	0·483	4·17
0·58	0·15	1·49	0·650	4·36
0·58	0·15	2·06	1·02	4·95
0·58	0·15	4·05	1·50	3·70

* IR = Initial rate of disappearance of linear dimer in mole l.$^{-1}$ hr.$^{-1}$. LD = Linear dimer.

TABLE 2. *Order in linear dimer at* 40°.

[LD] (mole l.$^{-1}$)	[Sb_2Cl_6] (mole l.$^{-1}$)	[HCl] (10^{-2} mole l.$^{-1}$)	IR (10^{-3} mole l.$^{-1}$ hr.$^{-1}$)	IR/[HCl][LD] (10^{-2} mole^{-1} l. hr.$^{-1}$)
0·373	0·15	1·48	0·406	7·36
0·581	0·15	1·49	0·65	7·53
0·70	0·15	1·55	0·872	8·04

TABLE 3. *Order in monomer at* 40°.

[M] † (mole l.$^{-1}$)	[Sb_2Cl_6] (mole l.$^{-1}$)	[HCl] (10^{-3} mole l.$^{-1}$)	IR † (10^{-4} mole l.$^{-1}$ hr.$^{-1}$)	IR/[M] (10^{-4} hr.$^{-1}$)
1·20	0·14	8·4	9·92	8·24
0·805	0·14	8·4	6·67	8·29
0·56	0·14	8·4	5·08	9·04

† IR = initial rate of appearance of linear dimer in mole l.$^{-1}$ hr.$^{-1}$. M = Monomer.

TABLE 4.

LD (mole l.$^{-1}$)	[Sb_2Cl_6] (mole l.$^{-1}$)	[HCl] (10^{-2} mole l.$^{-1}$)	IR * (10^{-3} mole l.$^{-1}$ hr.$^{-1}$)	Temp.
0·64	0·155	1·79	0·97	30°
0·64	0·155	1·67	1·75	40
0·64	0·155	1·90	4·69	55

* IR = Initial rate of disappearance of linear dimer in mole l.$^{-1}$ hr.$^{-1}$).

Spectra of solutions. Reacting systems were colourless during the period leading to the establishment of the monomer–linear dimer equilibrium. For those systems in which [Sb_2Cl_6] was greater than 0·21 mole l.$^{-1}$, the stationary period of monomer–linear dimer equilibrium was followed after several weeks by a slow decrease in volume as the cyclic dimer was formed, and at this stage the solutions became coloured. For these cases samples of the reaction mixture were sealed off in spectroscopic cells (*D*, Fig. 1), and the spectra were measured (Fig. 4).

DISCUSSION

Mechanism of Reaction.—The results show that antimony trichloride requires a cocatalyst for the activation of olefinic double bonds. With hydrogen chloride as cocatalyst, both the monomer and the linear dimer react to form the equilibrium mixture of monomer and linear dimer. The initial rate for the reaction of the linear dimer is of the first order in linear dimer and of the first order in hydrogen chloride, but the order in antimony trichloride is three. We believe that this high order is due to the fact that antimony trichloride helps to solvate the ion pairs formed by the addition of a proton to the olefin.

Since the antimony trichloride will most certainly be dimeric under the conditions of our experiments, we will write the following reaction scheme, which is analogous to that given for the reaction catalysed by stannic chloride–hydrogen chloride except that in the latter case the stannic salt did not help to solvate the ion pairs. We shall refer to reactions (*a*) as forward reactions, and to reactions (*b*) as reverse reactions.

$$3Sb_2Cl_6 + HCl + \underset{\text{Monomer}}{CH_2{:}CPh_2} \underset{b}{\overset{a}{\rightleftharpoons}} \{Me{\cdot}C^+Ph_2\ Sb_2Cl_7^-\}_{\mathbf{2Sb_2Cl_6}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\{Me{\cdot}C^+Ph_2\ Sb_2Cl_7^-\}_{\mathbf{2Sb_2Cl_6}} + CH_2{:}CPh_2 \underset{b}{\overset{a}{\rightleftharpoons}} \{Me{\cdot}CPh_2{\cdot}CH_2{\cdot}C^+Ph_2\ Sb_2Cl_7^-\}_{\mathbf{2Sb_2Cl_6}} \quad . \quad . \quad . \quad (2)$$

$$\{Me{\cdot}CPh_2{\cdot}CH_2{\cdot}C^+Ph_2\ Sb_2Cl_7^-\}_{\mathbf{2Sb_2Cl_6}} \underset{b}{\overset{a}{\rightleftharpoons}} \underset{\text{Linear dimer}}{Me{\cdot}CPh_2{\cdot}CH{=}CPh_2} + 3Sb_2Cl_6 + HCl \quad . \quad . \quad . \quad . \quad (3)$$

That the initial rate for the conversion of monomer into linear dimer is of the first order in monomer shows that the rate-determining step in the forward direction is reaction (1*a*). One would thus expect that the rate-determining step for the reverse reaction would be (1*b*). If this were so, the initial rate of the reverse reaction would depend on [linear dimer]$^{\frac{1}{2}}$, whereas in fact, it depends on [linear dimer],[1] which would require reaction (2*b*) to be the rate-determining step. We believe the explanation of these results to be as follows.

The orders in the reagents have been obtained from the initial rates of the forward and the reverse reactions. At zero time, the concentration of monomer will be equal to [initial monomer] for the forward reaction, but will be equal to zero for the reverse reaction. Thus the monomer ion, when formed from the monomer by reaction (1*a*), in the initial stages of the forward reaction, can undergo rapid conversion into the dimer ion by reaction (2*a*) because there will be a high concentration of monomer present, and the rate-determining step for the initial stages of the forward reaction will be reaction (1*a*). When the monomer ion is formed from the dimer ion by reaction (2*b*) in the initial stages of the reverse reaction, however, its conversion back into the dimer ion will be much slower because the concentration of monomer present will be negligibly small. Its reaction to monomer by reaction (1*b*), however, is independent of monomer concentration, and, hence, at these negligibly small monomer concentrations, every monomer ion produced by reaction (2*b*) will undergo conversion into monomer by reaction (1*b*). That is, the rate-determining step for the initial stages of the reverse reaction will be reaction (2*b*).

Thus we may write:

$$\begin{aligned}\text{Initial rate of forward reaction} &= k_f[\mathrm{M}][\mathrm{HCl}][\mathrm{Sb_2Cl_6}]^3\\ &= k_{1a}[\mathrm{M}][\mathrm{HCl}][\mathrm{Sb_2Cl_6}]^3,\end{aligned}$$

$$i.e.,\ k_f = k_{1a}.$$

$$\begin{aligned}\text{Initial rate of reverse reaction} &= k_r[\mathrm{LD}][\mathrm{HCl}][\mathrm{Sb_2Cl_6}]^3\\ &= \frac{k_{2b}k_{3b}}{k_{3a}}\cdot[\mathrm{LD}][\mathrm{HCl}][\mathrm{Sb_2Cl_6}]^3,\end{aligned}$$

$$i.e.,\ k_r = k_{2b}k_{3b}/k_{3a},$$

where M = monomer, and LD = linear dimer.

Thermodynamic Quantities for the Reaction.—In Table 5 we give the thermodynamic results for the reaction of linear dimer to monomer (reverse reaction). It is seen that the large amount of solvation of the ions has reduced $\Delta H_r^\ddagger$ to quite a low value; in fact it is only 0·6 kcal. mole^{-1} greater than the value of ΔH_r° (10·3 kcal. mole^{-1}), the endothermicity of the reverse reaction.

TABLE 5. *Results for the conversion of linear dimer into monomer* (*reverse reaction*).

k_r * 1·4	$\Delta G_r^\ddagger$ 21·0 (40°)	$\Delta H_r^\ddagger$ 10·9	$\Delta S_r^\ddagger$ −32·3 (40°)
	ΔG_r° 1·55 (39·9°) †	ΔH_r° 10·3 †	ΔS_r° 28·0 (39·9°) †
(10^{-2} mole^{-4} l.^{4} sec.$^{-1}$)	(kcal. mole^{-1})	(kcal. mole^{-1})	(cal. deg.$^{-1}$ mole^{-1})

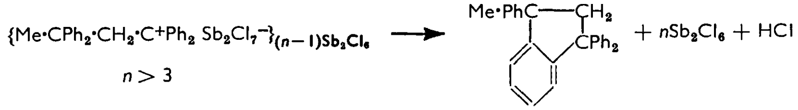
* Obtained from Fig. 3. † Obtained from results for forward reaction.[4]

Formation of Cyclic Dimer.—When [Sb_2Cl_6] is less than 0·21 mole l.$^{-1}$, the monomer–linear dimer equilibrium is reached without a colour developing and no further change occurs during 12 months. When [Sb_2Cl_6] exceeds 0·21 mole l.$^{-1}$, the equilibrium mixture undergoes a very slow change to cyclic dimer. For example, when [Sb_2Cl_6] = 0·3 mole l.$^{-1}$, [linear dimer] = 0·78 mole l.$^{-1}$, and [HCl] = $2{\cdot}33 \times 10^{-2}$ mole l.$^{-1}$, the monomer–linear dimer equilibrium is attained in 20 hours, and the dilatometer reading remains constant for a further 100 hours, after which the volume very slowly decreases, a colour develops, and analysis shows that cyclic dimer is being formed. Thus it is seen that for antimony trichloride–hydrogen chloride systems, the rate at which linear dimer is converted into cyclic dimer is very much slower than its rate of conversion into monomer.

Spectrum of Solution.—The antimony trichloride–hydrogen chloride catalyst differs from all those which we have used previously for this reaction, in that it brings about the monomer–linear dimer equilibration without the solution's showing the characteristic spectrum of the carbonium ion. This must mean that the ion pair, consisting of the carbonium ion and the $Sb_2Cl_7^-$ counter-ion and solvated by antimony trichloride, is much more unstable than the ion pairs obtained in the other catalytic systems we have studied.

For those systems in which [Sb_2Cl_6] exceeds 0·21 mole l.$^{-1}$, we find that, although no colour is present in the solution during the attainment of the monomer–linear dimer equilibrium, and for the stationary period of this equilibrium, a colour develops as the solution undergoes the further contraction to form cyclic dimer. This colour (see Fig. 4) is characteristic of the monomer in a weak acid medium;[6] it is not due to the formation of cyclic dimer, since the system cyclic dimer–antimony trichloride–hydrogen chloride is colourless and shows no change in volume with time.

It appears that there is a slow increase in the number of antimony trichloride molecules solvating the ion pairs, the final extent of solvation being greater the greater the antimony trichloride concentration. Monomer–linear dimer equilibration can occur at reasonable rates for a degree of solvation which is, however, not sufficient to give a concentration of ion pairs which is visible. When [Sb_2Cl_6] is greater than 0·21 mole l.$^{-1}$, the monomer–linear dimer equilibration is completed during the early stages of the ion-pair solvation. However, solvation continues slowly until the ion-pair concentration is high enough to be visible, and at this stage the concentration of linear dimer ions is also high enough for them to be converted into cyclic dimer by reaction (4) at a measurable, though extremely slow, rate. We found earlier, for the stannic chloride–hydrogen chloride system,[3] that cyclisation of the linear dimer ion is associated with a large negative entropy term, and much higher concentrations of linear dimer ion are required in order to obtain a reasonable rate of conversion of linear dimer into cyclic dimer than are necessary for its conversion into monomer.



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[6] Evans, Jones, and Thomas, *J.*, 1957, 104.

Since the initial rate of conversion of linear dimer into monomer can depend on antimony trichloride concentration to as high an order as 3 without the solution's being coloured, it seems that when the colour finally becomes visible the ion pairs must be enclosed in very many molecules of antimony trichloride, almost as though they are in a medium of liquid antimony trichloride. It is interesting, in this connexion, that in the absence of benzene—that is, in liquid antimony trichloride at its melting point (73°)—the reaction solutions are intensely coloured immediately they are made up.

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