580. *The Activation of Carbon–Carbon Double Bonds by Cationic Catalysts. Part V.*[1] *The Dimerization of* 1 : 1-*Diphenylethylene in the System Benzene–Stannic Chloride–Water.*

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Dimerization of 1 : 1-diphenylethylene in benzene–stannic chloride–water has been studied by a dilatometric method. There is no reaction in the absence of water, and the true catalyst is stannic chloride dihydrate. Non-reacting systems are colourless, but reacting systems have an absorption spectrum similar to that given by this olefin in various acid solutions.

IN earlier Parts of this series [1] we reported the dimerization of 1 : 1-diphenylethylene and its derivatives, using trichloroacetic acid and iodine as catalysts. This work has now been extended by using stannic chloride–water as catalyst.

EXPERIMENTAL

Materials.—Stannic chloride was prepared by direct combination of the elements,[2] or by a new technique in which fused stannous chloride was electrolyzed in a Pyrex glass apparatus under a high vacuum (see Fig. 1). Anhydrous " AnalaR " stannous chloride was distilled from *A* into the electrolytic cell, *C*, under a high vacuum after the whole apparatus had been baked out. Vessel *A* was sealed off at *X*, the stannous chloride fused by the heater *H*, and a 12 v D.C. potential applied across the terminals T_1 and T_2 (T_1 led to a gas-carbon rod which served as anode). Bubbles of stannic chloride vapour rose from the anode. The first runnings were pumped out and then the system was sealed off at *Y*. Electrolysis was continued until sufficient stannic chloride had been condensed in the sample holder, *S*, which was removed from the system by being sealed off at *Z*.

FIG. 1.

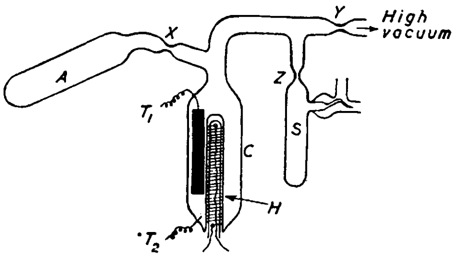
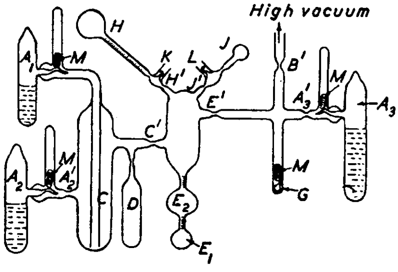


FIG. 2.



1 : 1-Diphenylethylene (from Messrs. Mersey Chemicals Limited) was fractionated at atmospheric pressure from potassium hydroxide pellets through a 30 cm. Hempel column packed with glass rings. The fraction boiling at 268—270° was collected and distilled under a high vacuum in an all glass apparatus. " AnalaR " benzene was further refined by standard methods, and, where the utmost purity was required, was outgassed under a high vacuum and distilled over a bright sodium film. Solutions containing a known concentration of water in benzene were prepared by saturating purified benzene with distilled water in thermostats, the known data for the solubility of water in benzene [3] being used.

Procedure.—*Method A*. Dilatometers were filled by means of an apparatus illustrated in Fig. 2. Vessels A_1, A_2, and A_3 contained stannic chloride, 1 : 1-diphenylethylene, and benzene respectively, each introduced by high-vacuum distillation. *G* is a calibrated bulb filled under a high vacuum with a known volume of stannic chloride. The apparatus was well baked out under a high vacuum and then sealed off at *B'*. The monomer was distilled from

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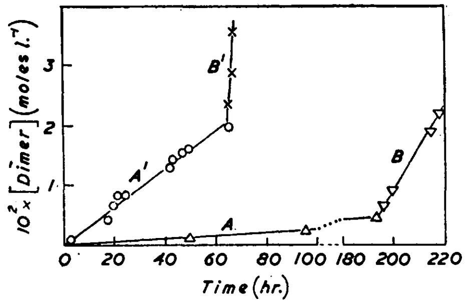
[1] Parts I—IV, Evans, Jones, and Thomas, *J.*, 1955, 1824; Evans, N. Jones, P. M. S. Jones, and Thomas, *J.*, 1956, 2757; Evans, P. M. S. Jones, and Thomas, *J.*, 1957, 104, 2095.

[2] Baxter and Starkweather, *J. Amer. Chem. Soc.*, 1938, **44**, 288.

[3] Internat. Crit. Tables, Vol. III, p. 389.

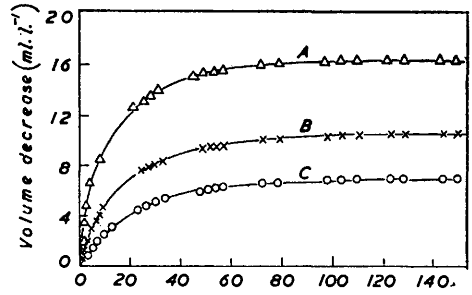
A_2 to C after the connecting capillary had been broken magnetically (M), and the system was sealed off at A_2'. The capillary A_1 was broken and the stannic chloride distilled through the monomer in C and condensed in D, which was then sealed off. This was done in order to remove the last traces of impurity from the olefin; the amount of dimerization produced by this treatment was negligible, since the impurity (*i.e.*, co-catalyst) remaining at this stage was so small. The treated monomer was distilled into the calibrated vessel E_1 so that its meniscus lay in the lower graduated stem, and the system sealed off at C'. The capillary at A_3 was then broken and benzene distilled into the calibrated vessel E_2 to reach some level in the upper graduated stem. The system was sealed off at A_3'. Finally the bulb G was broken and the contents distilled into the benzene–monomer mixture. The system was sealed off at E', the three components thoroughly mixed by agitation of the apparatus, and the dilatometer H and the optical cell J filled to suitable levels and sealed off at H' and J'. After 2—3 days, water was introduced into the dilatometer and into the optical cell by sealing a small bulb containing a known quantity of water vapour, or of benzene saturated with water, on to the side tubes K and L, and breaking the fragile capillaries with a magnetically operated breaker. By thorough agitation of the system before re-sealing of the dilatometer and the optical cell, solutions were obtained in each having the same, known, water concentration. Dilatometers and optical cells were filled in this way with solutions having various, known concentrations in 1 : 1-diphenylethylene, stannic chloride, and water.

FIG. 3. *Initial rates for highly purified systems at* 39·9°.



A, Initial [monomer] 1·10 mole l.$^{-1}$; [stannic chloride] 4·73 × 10^{-3} mole l.$^{-1}$. B, As A with water (7·74 × 10^{-3} mole l.$^{-1}$) added. A', Initial [monomer] 1·22 mole l.$^{-1}$; [stannic chloride] 1·86 × 10^{-1} mole l.$^{-1}$. B', As A' with water (1·47 × 10^{-3} mole l.$^{-1}$) added.

FIG. 4. *Volume change during reaction at* 39·9°.



Total [$SnCl_4$] 0·172 mole l.$^{-1}$; [added H_2O] 1·22 × 10^{-2} mole l.$^{-1}$; initial [monomer] (A) 1·65, (B) 1·10, (C) 0·77 mole l.$^{-1}$.

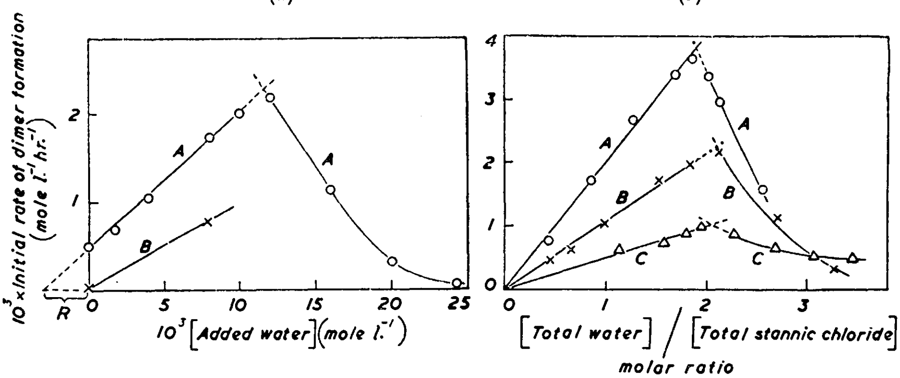
Method B. Other dilatometers were filled by mixing varying quantities of monomer–benzene, stannic chloride–benzene and water–benzene master solutions by the method described in Part I[1].

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 accompanying changes in the spectrum were measured in the optical cells by a Unicam S.P. 500 Spectrophotometer. The rate of change of volume was converted into mole l.$^{-1}$ hr.$^{-1}$ of dimer produced (as described in Parts I and II [1]), by using the following values for the volume change accompanying the complete conversion of 1 mole of monomer into ½ mole of dimer : 11·95 ml. at 30·3°, 11·70 ml. at 39·9°, and 12·60 ml. at 55·0°, which we have found for the conditions obtaining in this present work.

RESULTS

When olefin and stannic chloride were mixed as in method A, the reaction rate was negligible, (Fig. 3, curve A). On introduction of water to such a system (provided the [water]/[total stannic chloride] molar ratio was not much greater than 2), a very marked acceleration in the rate was obtained (Fig. 3, curve B). It is clear, therefore, that water is necessary for the reaction, and that the small reaction occurring in the rigorously dried systems is due to the trace of water still remaining in the reagents. It being established that a co-catalyst is necessary, the systems containing various amounts of water were made up by method B, in which much less rigorous drying of the reagents was involved. Systems containing benzene, olefin, stannic chloride, and water, made by this method, gave reaction curves of the type shown in Fig. 4, the volume decreasing until a constant value was obtained. (No volume change occurred in the absence of monomer.) The product of the reaction was separated as described in Part I, and it was again found to be solely 1 : 1 : 3 : 3-tetraphenylbut-1-ene (see also Schoepfle and Ryan[4]). Further, the amount of dimer obtained from the equilibrium solutions agreed to within ±5% with that expected from the observed volume change (see Part I). Initial rates of reaction were found from the initial slopes of the reaction curves, and the dependence of rate on concentration of added water for constant [total stannic chloride] and constant [olefin] is shown for a typical case in Fig. 5*a*, curve *A*. It is seen that the initial rate of dimerization in absence of added water, although small, is finite ($4{\cdot}7 \times 10^{-4}$ mole $l.^{-1}$ $hr.^{-1}$). Systems of the same olefin and stannic chloride concentration purified by method *A*, however, show no such intercept, (see Fig. 5*a*, curve *B*). It is thus clear that the finite intercept on the ordinate in curve *A*, for systems made up by method *B*, is due to residual water. We have therefore extrapolated the curve back to the axis and get a value of $3{\cdot}0 \times 10^{-3}$ mole $l.^{-1}$ for the residual water in this experiment. In this way we find that the maximum rate occurs for a [total water]/[total stannic chloride] molar ratio of $(3{\cdot}0 + 11{\cdot}5)/7{\cdot}0 = 2{\cdot}1$. In Fig. 5*b* are shown results for different stannic chloride concentrations : the maximum rate of dimerization occurs at a [total water]/[total stannic chloride] molar ratio of $2 \pm 0{\cdot}1$. Thus the true catalyst in this system is $SnCl_4,2H_2O$.

FIG. 5. *Variation in initial rate at* 39·9° *with variation in water concentration.*



(5*a*) Curve *A*, Initial [monomer] 1·13 mole $l.^{-1}$; [Total stannic chloride] $7{\cdot}01 \times 10^{-3}$ mole $l.^{-1}$. R = Residual water in the reagents (obtained by extrapolation) = $3{\cdot}0 \times 10^{-3}$ mole $l.^{-1}$. Curve *B*, Highly purified systems; data obtained from curves *A* and *B* of Fig. 3.

(5*b*) Initial [monomer] 1·13 mole $l.^{-1}$; [Total stannic chloride] (*A*) $9{\cdot}21 \times 10^{-3}$, (*B*) $7{\cdot}01 \times 10^{-3}$, (*C*) $4{\cdot}84 \times 10^{-3}$ mole $l.^{-1}$.

In Fig. 6 we plot log (initial rate) against log [initial monomer] for constant [total stannic chloride] and constant [total water] : the order in monomer is $2{\cdot}3 \pm 0{\cdot}3$. In Fig. 6 we also plot log (initial rate) against log [$SnCl_4,2H_2O$] for constant [initial monomer] and constant [total water]/[total stannic chloride] molar ratio of 2, and find the order in $SnCl_4,2H_2O$ to be $2{\cdot}0 \pm 0{\cdot}5$. Also in Fig. 6 we plot log (initial rate) against log [total stannic chloride] for systems in which the [total water]/[total stannic chloride] molar ratio is not greater than 2 : over a considerable range of stannic chloride concentration, the order in [total stannic chloride] is $0{\cdot}9 \pm 0{\cdot}1$.

The values of $[M]_e$ and $[D]_e$ (the concentrations of monomer and dimer at equilibrium) have been obtained for solutions of different initial monomer concentrations as described in Part I. In Fig. 7 the plot of log $[D]_e$ against log $[M]_e$ is given, and the slope of the line found to be

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

TABLE 1.

Temp.	[Initial monomer] (mole l.$^{-1}$)	[Total stannic chloride] (10^{-3} mole l.$^{-1}$)	[Total water] (10^{-3} mole l.$^{-1}$)	k_t * (10^{-3} mole^{-3} l.^{3} sec.$^{-1}$)	K (mole^{-1} l.)
39·9°	1·13	4·84	9·41	9·1	11·1
39·9	1·13	7·10	14·8	9·5	10·9
39·9	1·13	8·21	17·3	11·8	11·6
39·9	1·65	172	15·2	9·2	11·0
			Mean	9·9	11·2

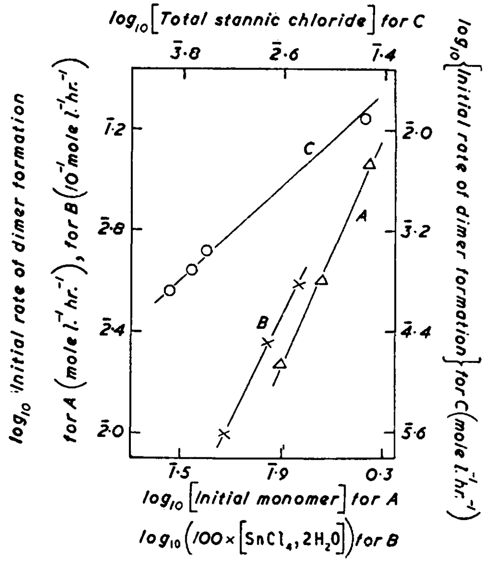
* k_t is evaluated in terms of the number of moles per l. of dimer appearing per second.

TABLE 2.

K (mole^{-1} l.)	$-\Delta H^\circ$ (kcal. mole^{-1})	$-\Delta G^\circ$ (kcal. mole^{-1})	$-\Delta S^\circ$ (cal. mole^{-1} deg.$^{-1}$)
19·9 ± 0·4 (30·3°)	10·5 ± 0·5	1·8 (30·3°)	28·7 (30·3°)
11·2 ± 0·4 (39·9°)			
5·4 ± 0·2 (55·0°)			

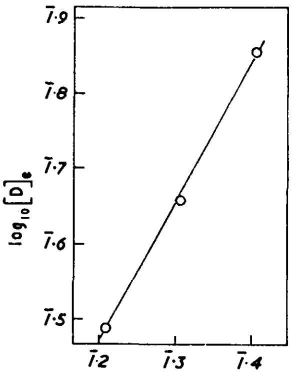
1·9 ± 0·1, showing that $[D]_e/[M]_e^2 = K$. These equilibrium constants, K, are found to be independent of the [total water] and [total stannic chloride] present (see Table 1). They have been determined for three temperatures (see Table 2), and the plot of log K against $1/T$ has been used to find the exothermicity of the reaction; the value obtained ($-\Delta H^\circ$) from the slope of this line is 10·5 ± 0·5 kcal. mole^{-1} (see Table 2). The values of ΔG° and ΔS° for this dimerization are also given in Table 2.

FIG. 6.



$A\left\{\begin{array}{l}\text{[Stannic chloride] } 1{\cdot}76 \times 10^{-1} \text{ mole l.}^{-1} \\ \text{[Added water] } 1{\cdot}25 \times 10^{-2} \text{ mole l.}^{-1}\end{array}\right\}$ at 39·9°.
B [Monomer] 1·13 mole l.$^{-1}$ at 39·9°.
$C\left\{\begin{array}{l}\text{[Monomer] } 1{\cdot}13 \text{ mole l.}^{-1} \\ \text{[Total water] } 5{\cdot}0 \times 10^{-3} \text{ mole l.}^{-1}\end{array}\right\}$ at 39·9°.

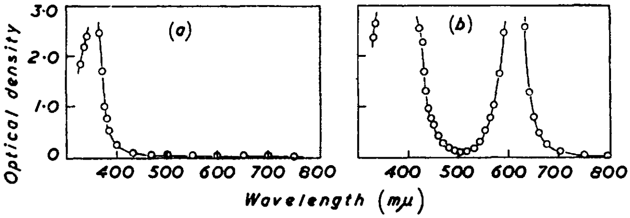
FIG. 7. *Relation between the equilibrium concentrations of monomer and dimer at* 39·9°.



All the solutions studied were seen to be homogeneous, and the results were very reproducible. For example, a practically two-fold change in the stannic chloride concentration gave a value of 2, constant to within ±5%, for the [total water]/[total stannic chloride] molar ratio at the maximum rate of dimerization.

We have also examined the spectra of these solutions, since it is important to know whether stannic chloride can interact with the olefin double bond in the absence of co-catalyst to give a coloured species, and, further, whether the reacting system is spectroscopically different from the non-reacting system. For these experiments we used concentrations of stannic chloride some 20—40 times greater than applying to Fig. 3, curve *A*, but, even so, in the rigorously purified systems there was no detectable colour (see Fig. 8*a*). For this system the reaction rate is shown in Fig. 3, curve *A′*. (The fact that the slope of curve *A′* is greater than that of curve *A* is due, of course, to the very much greater stannic chloride concentration present in the former case.) On addition of water, the reaction rate increased very greatly (Fig. 3, curve *B′*), and simultaneously the spectrum changed to give absorption in the violet end of the visible region and a peak in the 600 mμ region, the solution now appearing green (see Fig. 8*b*).

FIG. 8.



(*a*) Spectrum of system given in Fig. 3, curve *A′*. (*b*) Spectrum of system given in Fig. 3, curve *B′*.

DISCUSSION

Friedel–Crafts catalysts do not polymerize olefins unless a co-catalyst, *e.g.*, water, is present. This has been shown for boron trifluoride,[5] titanium tetrachloride,[6] and stannic chloride.[7] The work described in this paper shows that 1 : 1-diphenylethylene is not dimerized by stannic chloride in benzene, but that addition of small traces of water brings about this reaction. Maximum rate of dimerization occurs when the [total water]/[total stannic chloride] molar ratio is 2; this was also found by Colclough [8] for the polymerization of styrene in styrene–stannic chloride–1 : 2-dichloroethane–water.

Any mechanism put forward for the dimerization of 1 : 1-diphenylethylene in benzene–stannic chloride–water must account for the following observations. The initial rate of dimerization is (*a*) of second order in monomer, (*b*) of second order in [$SnCl_4,2H_2O$], (*c*) of first order in [total stannic chloride] provided the molar ratio [total water]/[total stannic chloride] < 2, and (*d*) of first order in [total water], provided the molar ratio [total water]/[total stannic chloride] < 2. 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, D dimer, and Solv. one molecule of either $SnCl_4$ or $SnCl_4,2H_2O$:

$$M + SnCl_4,2H_2O + Solv. \underset{b}{\overset{a}{\rightleftharpoons}} \{HM^+(SnCl_4,H_2O,OH)^-\}_{Solv.} \quad . \quad . \quad . \quad (1)$$

$$M + \{HM^+(SnCl_4,H_2O,OH)^-\}_{Solv.} \underset{b}{\overset{a}{\rightleftharpoons}} \{HD^+(SnCl_4,H_2O,OH)^-\}_{Solv.} \quad . \quad . \quad . \quad (2)$$

$$\{HD^+(SnCl_4,H_2O,OH)^-\}_{Solv.} \underset{b}{\overset{a}{\rightleftharpoons}} D + SnCl_4,2H_2O + Solv. \quad . \quad . \quad . \quad (3)$$

This mechanism will account for the results if we make the following assumptions: (*a*) reaction 2*a* is the rate-controlling step in the forward direction; (*b*) when [total water]/[total stannic chloride < 2, the water is all in the form $SnCl_4,2H_2O$ and the excess of stannic chloride is present as $SnCl_4$; (*c*) $SnCl_4$ and $SnCl_4,2H_2O$ have equal or nearly equal solvating

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[5] Evans and Polanyi, *J.*, 1947, 252; Evans and Meadows, *Trans. Faraday Soc.*, 1950, **46**, 327.

[6] Plesch, Polanyi, and Skinner, *J.*, 1947, 257.

[7] Norrish and Russell, *Trans. Faraday Soc.*, 1952, **48**, 91.

[8] Colclough, Chem. Soc. Symp. on Friedel–Crafts Reaction, Leeds, May, 1955; *Chem. and Ind.*, 1955, 741.

powers in respect of the ion pairs involved; and (*d*) when [total water]/[total stannic chloride] >2, either the excess of water retards the reaction, or if a hydrate of stannic chloride higher than the dihydrate is formed, it is much less efficient as a catalyst. If these assumptions are made, the initial rate of dimerization, as observed experimentally, is given by:

$$\begin{aligned}\text{Initial Rate} &= k_{2a}[\{\text{HM}^+(\text{SnCl}_4,\text{H}_2\text{O},\text{OH})^-\}_{\text{Solv.}}][\text{M}] \\ &= k_{2a}\cdot\frac{k_{1a}}{k_{1b}}[\text{SnCl}_4,2\text{H}_2\text{O}][\text{Solv.}][\text{M}]^2 \quad . \quad . \quad . \quad . \quad . \quad (4)\end{aligned}$$

This expression is consistent with our results, since, when [total water]/[total stannic chloride] is equal to or less than 2, then [Solv.] is equal to $[\text{SnCl}_4,2\text{H}_2\text{O}] + [\text{SnCl}_4]$. But $[\text{SnCl}_4]$ is equal to [total stannic chloride] $-$ $[\text{SnCl}_4,2\text{H}_2\text{O}]$, and therefore [Solv.] is equal to [total stannic chloride]. Thus equation (4) becomes:

$$\text{Initial Rate} = k_{2a}\frac{k_{1a}}{k_{1b}}[\text{SnCl}_4,2\text{H}_2\text{O}][\text{total stannic chloride}][\text{M}]^2$$

So when [total water] is constant, $[\text{SnCl}_4,2\text{H}_2\text{O}]$ is constant, and the initial rate will vary linearly with [total stannic chloride], giving the observed first-order dependence in stannic chloride; further, when [total stannic chloride] is constant, the initial rate will vary linearly with $[\text{SnCl}_4,2\text{H}_2\text{O}]$, *i.e.*, with [total water], giving the observed first-order dependence on water. Again, when [total water]/[total stannic chloride] is equal to 2, [Solv.) is equal to $[\text{SnCl}_4,2\text{H}_2\text{O}]$, and equation (4) becomes:

$$\text{Initial Rate} = k_{2a}\cdot\frac{k_{1a}}{k_{1b}}[\text{SnCl}_4,2\text{H}_2\text{O}]^2[\text{M}]^2$$

which agrees with the observed second-order dependence of initial rate on $[\text{SnCl}_4,2\text{H}_2\text{O}]$ when the [total water]/[total stannic chloride] molar ratio is 2.

Since for systems in which the [total water]/[total stannic chloride] molar ratio is $\leqslant 2$, [Solv.] is equal to [total stannic chloride], the velocity constant, k_f, for the dimerization reaction has been evaluated from the expression:

$$\text{Initial rate} = k_f[\text{SnCl}_4,2\text{H}_2\text{O}][\text{total stannic chloride}][\text{M}]^2,$$

where $k_f = k_{2a}k_{1a}/k_{1a} = k_{2a}K_1$.

The value of k_f at 39·9° was found to be $1{\cdot}01 \times 10^{-2}$ mole^{-3} l.^{3} sec.$^{-1}$ (see Table 1).

The assumption that $\text{SnCl}_4,2\text{H}_2\text{O}$ and SnCl_4 help in solvating the ion pairs formed in the poorly ionizing benzene solution is supported by the fact that solvation of a similar type appears to occur also (*a*) with trichloroacetic acid in the dimerization of 1 : 1-diarylethylenes when the acid is used as catalyst (Parts I and II [1]) and (*b*) with mercuric chloride in the ionization of triarylmethyl halides by mercuric chloride in chlorobenzene and benzene.[9] It is surprising, however, that in order to interpret our results we have to assume that the solvating powers of SnCl_4 and of $\text{SnCl}_4,2\text{H}_2\text{O}$ are practically the same. Further experiments to elucidate this are in progress, with hydrogen chloride instead of water as co-catalyst.

The equilibrium constant, K, will be given by the relation:

$$K = \frac{k_{1a}}{k_{1b}}\cdot\frac{k_{2a}}{k_{2b}}\cdot\frac{k_{3a}}{k_{3b}} = K_1K_2K_3$$

The values of K, $\Delta G°$, $\Delta H°$, and $\Delta S°$ obtained for this dimerization reaction (see Table 2) agree very well with those obtained in Part I for the same reaction in benzene–trichloroacetic acid [$\Delta G°$ (34°) $= -1{\cdot}69$ kcal. mole^{-1}, $\Delta H° = -10{\cdot}1$ kcal. mole^{-1}, $\Delta S°$ (34°) $= -27{\cdot}4$ cal. mole^{-1} deg.$^{-1}$]. Holmes and Tyrrall [10] have studied this equilibrium in carbon

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[9] Bayles, Evans, and Jones, *J.*, 1957, 1021.

[10] Holmes and Tyrrall, *Trans. Faraday Soc.*, 1956, **52**, 47.

tetrachloride–stannic chloride–hydrogen chloride by a calorimetric method, and obtain the values $\Delta H^\circ = -12{\cdot}1$ kcal. mole^{-1}, $K(35^\circ) = 17{\cdot}1$ mole^{-1} l.

The presence of the ionic intermediates should be detectable spectroscopically if reaction (2*a*) is the rate-determining step, since the diphenylmethyl carbonium ion absorbs light in the visible region at 431 mμ.[11] It is significant in this respect that those systems in which dimerization is proceeding are coloured and absorb light in this region, whereas anhydrous, rigorously dried systems in which the rate of dimerization is negligible are colourless (see Fig. 8). The absorption (at 625 mμ) is similar to that for 1 : 1-diarylethylenes in various acid solutions which we attribute to the presence of a π-complex (see Part III [1]).

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[11] Evans, *J. Appl. Chem.*, 1951, **1**, 240.