

181. The Activation of Carbon-Carbon Triple Bonds by Cationic Catalysts. Part II.¹ The Interaction of Stannic Chloride with Phenylacetylene and with Pent-1-yne in Benzene.

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Phenylacetylene and pent-1-yne react with stannic chloride in benzene to give a complex containing two molecules of the acetylene and one of stannic chloride. The presence of hydrogen chloride does not affect this reaction but brings about the production of a trace of polymer containing conjugated double bonds.

WE have previously investigated the action of trichloroacetic acid on phenylacetylene;¹ in this Paper we study the action of stannic chloride on phenylacetylene and on pent-1-yne with and without hydrogen chloride present.

EXPERIMENTAL AND RESULTS

Materials.—Phenylacetylene was purified by the method described earlier.¹ It was dried under vacuum by prolonged storage over barium oxide followed by distillation. When rigorously dried material was required, it was purified as follows. Tri-isobutylaluminium was added in successive small quantities using the high vacuum technique employed earlier for the addition of titanium tetrachloride to olefins.² The system became yellow and addition of alkyl was continued until evolution of gas ceased; it was then outgassed and repeated distillation under vacuum gave the acetylene freed from all traces of tri-isobutylaluminium. The infrared spectrum of the acetylene after this treatment was identical with that before treatment. When phenylacetylene, dried in this way, was mixed with stannic chloride, a pale yellow solution resulted, whereas the addition of stannic chloride to the undried acetylene produced a black solution and a solid precipitate. The addition of both stannic chloride and tri-isobutylaluminium to the purified acetylene resulted in an immediate red-brown precipitate and the solution rapidly became viscous.

These experiments show that the phenylacetylene after treatment with tri-isobutylaluminium (*a*) has not been attacked by the alkyl, (*b*) is drier than before treatment, and (*c*) contains no alkylaluminium, or does so in negligible concentration.

Pent-1-yne was rigorously dried by this same technique using triethylaluminium as the desiccant. Benzene,² stannic chloride,³ and hydrogen chloride⁴ were purified as described earlier.

Triethylaluminium and tri-isobutylaluminium (given by Petrochemicals Ltd., Carrington) were transferred under dry nitrogen into a high vacuum system where they were degassed and passed into a series of bulbs which were then sealed.

Procedure.—A solution of the acetylene in benzene was made up and introduced into dilatometers under high vacuum conditions.³ Known amounts of stannic chloride and hydrogen chloride were added⁴ and the reaction was followed dilatometrically as described earlier. Reaction products were obtained either from reaction solutions which had proceeded to completion or, when large quantities were required for analysis, large dilatometers were used. Solvent and residual acetylene were distilled off leaving the reaction product—a blackish solid from the reaction of phenylacetylene and a brown liquid from the reaction of pent-1-yne. Distillation under vacuum of the liquid product from pent-1-yne gave a colourless oil, b. p. 60°/0.05 mm., and a black residue remained (~5%). The solid product from phenylacetylene was not further purified. Both products readily absorbed moisture if they were exposed to the atmosphere.

Elemental Analysis.—Analysis of the reaction products showed the presence of tin.

Product from phenylacetylene. Found: C, 40.1; H, 2.7; Cl, 33.6. $C_{16}H_{12}SnCl_4$ requires C, 41.3; H, 2.6; Cl, 30.5%.

¹ Part I, Evans, Owen, and Phillips, *J.*, 1964, 5021.

² Evans and Owen, *J.*, 1959, 4123.

³ Evans and Lewis, *J.*, 1957, 2975.

⁴ Evans and Lewis, *J.*, 1959, 1946.

Colourless product from pent-1-yne. Found: C, 31.2; H, 4.4; Cl, 32.3. $C_{10}H_{16}SnCl_4$ requires C, 30.25; H, 4.0; Cl, 35.8%.

Molecular Weight Determined Cryoscopically in Benzene.—Product from phenylacetylene. Found: 450 ± 40 . $C_{16}H_{12}SnCl_4$ requires 464.7.

Product from Pent-1-yne. Found: 407 ± 50 . $C_{10}H_{16}SnCl_4$ requires 396.7.

Spectra.—The salient features of the infrared spectra of the products from phenylacetylene and from pent-1-yne are listed in Table I.

TABLE I.

Infrared spectra of reaction products: (A) from phenylacetylene; (B) from pent-1-yne.					
A (cm. ⁻¹)	B (cm. ⁻¹)	Assignment	A (cm. ⁻¹)	B (cm. ⁻¹)	Assignment
3090		R ¹ R ² C=CH ₂	1584		C=C and Ph conjugated
	3040	R ¹ R ² C=CHR ³	888		R ¹ R ² C=CH ₂
1626		C=C and Ph conjugated		765	R ¹ R ² C=CHR ³
	1603	C=C conjugated			

Kinetic Measurements.—Orders of reaction. Hydrogen chloride was found to have no effect on the initial rate of volume contraction (R_i), (see Tables 2A and B). The colour of reaction solutions was markedly affected, however; in the absence of hydrogen chloride the solutions containing pent-1-yne remained colourless, and those containing phenylacetylene were yellow, but in the presence of hydrogen chloride, the solutions became purple-black and dark brown, respectively.

TABLE 2A.

Effect of hydrogen chloride on initial reaction rate at 30°.

$[PhC\equiv CH]_i = 1.09$ mole l. ⁻¹ . $[SnCl_4]_i = 1.04 \times 10^{-1}$ mole l. ⁻¹ .					
$10^3[HCl]_i$ (mole l. ⁻¹)	0	5.41	10.0	50.8	98.0
10^2R_i * (ml. l. ⁻¹ hr. ⁻¹)	6.53	6.02	6.13	6.26	6.04

TABLE 2B.

Effect of hydrogen chloride on initial reaction rate at 30°.

$[Pent-1-yne]_i = 1.04$ mole l. ⁻¹ . $[SnCl_4]_i = 8.5 \times 10^{-2}$ mole l. ⁻¹ .					
$10^4[HCl]_i$ (mole l. ⁻¹)	0	9.95	23.0	54.5	115.0
10^2R_i * (ml. l. ⁻¹ hr. ⁻¹)	3.95	3.70	4.19	4.32	4.22

* R_i = Initial rate of reaction.

The initial rate of volume contraction was found at constant stannic chloride concentration to be linear within $\pm 9\%$ with respect to the initial concentration of the acetylene (see Tables 3A and B).

TABLE 3A.

Order of reaction in phenylacetylene at 30°.

$[SnCl_4]_i = 1.05 \times 10^{-1}$ mole l. ⁻¹			
$[PhC\equiv CH]_i$ (mole l. ⁻¹)	10^2R_i (ml. l. ⁻¹ hr. ⁻¹)	$10^2R_i/[PhC\equiv CH]_i$ (ml. mole ⁻¹ hr. ⁻¹)	$10^2R_i/\{[PhC\equiv CH]_i - [SnCl_4]_i\}$ (ml. mole ⁻¹ hr. ⁻¹)
0.96	5.75	5.99	6.69
1.09	6.53	5.99	6.60
1.44	9.94	6.90	7.42
1.85	13.0	7.03	7.45

TABLE 3B.

Order of reaction in pent-1-yne at 30°.

$[SnCl_4]_i = 9.0 \times 10^{-2}$ mole l. ⁻¹ .			
$[Pent-1-yne]_i$ (mole l. ⁻¹)	10^2R_i (ml. l. ⁻¹ hr. ⁻¹)	$10^2R_i/[pent-1-yne]_i$ (ml. mole ⁻¹ hr. ⁻¹)	$10^2R_i/\{[pent-1-yne]_i - [SnCl_4]_i\}$ (ml. mole ⁻¹ hr. ⁻¹)
1.01	7.85	7.77	8.53
1.41	10.9	7.73	8.26
1.81	16.7	9.23	9.70

The order of reaction in stannic chloride was found to be 1.0 ± 0.1 and in the presence of excess of acetylene, the total volume contraction was directly proportional to the stannic chloride concentration (see Tables 4A and B).

TABLE 4A.

Order of reaction in stannic chloride at 30°.

$$[\text{PhC}\equiv\text{CH}]_i = 1.08 \pm 0.2 \text{ mole l.}^{-1}.$$

$10^2[\text{SnCl}_4]_i$ (mole l. ⁻¹)	10^2R_i (ml. l. ⁻¹ hr. ⁻¹)	$10R_i/[\text{SnCl}_4]_i$ (ml. mole ⁻¹ hr. ⁻¹)	Volume decrease (ml. l. ⁻¹)	Volume decrease/ $[\text{SnCl}_4]_i$ (ml. mole ⁻¹)
4.94	2.64	5.34	1.74	35.2
6.94	4.21	6.08	2.47	35.7
8.12	4.20	5.17	2.87	35.3
10.4	6.26	6.02	3.71	35.7
12.3	6.93	5.63	4.30	35.0
15.7	8.75	5.57	5.64	35.9
18.5	11.4	6.16	6.48	35.0

TABLE 4B.

Order of reaction in stannic chloride at 30°.

$$[\text{Pent-1-yne}]_i = 1.0 \pm 0.03 \text{ mole l.}^{-1}.$$

$10^2[\text{SnCl}_4]_i$ (mole l. ⁻¹)	10^2R_i (ml. l. ⁻¹ hr. ⁻¹)	$10R_i/[\text{SnCl}_4]_i$ (ml. mole ⁻¹ hr. ⁻¹)	Volume decrease (ml. l. ⁻¹)	Volume decrease/ $[\text{SnCl}_4]_i$ (ml. mole ⁻¹)
5.31	2.92	5.5	1.88	35.4
5.36	2.72	5.08	1.78	33.2
6.20	3.50	5.65	2.12	34.2
8.16	4.11	5.03	2.86	35.1
8.50	4.08	4.8	2.92	34.4

TABLE 5A.

Temperature dependence of initial rate of reaction.

$$[\text{PhC}\equiv\text{CH}]_i = 1.06 \text{ mole l.}^{-1}, \quad [\text{SnCl}_4]_i = 6.9 \times 10^{-2} \text{ mole l.}^{-1}.$$

Temp. (°c)	20	30	40	50
10^2R_i (ml. l. ⁻¹ hr. ⁻¹)	2.36	4.21	8.25	15.2
Volume decrease (ml. l. ⁻¹)	—	2.47	2.42	2.5

TABLE 5B.

Temperature dependence of initial rate of reaction.

$$[\text{Pent-1-yne}]_i = 1.03 \text{ mole l.}^{-1}, \quad [\text{SnCl}_4]_i = 6.2 \times 10^{-2} \text{ mole l.}^{-1}.$$

Temp. (°c)	20	30	40	55
10^2R_i (ml. l. ⁻¹ hr. ⁻¹)	1.7	3.5	6.6	17.1
Volume decrease (ml. l. ⁻¹)	—	2.12	2.12	2.16

When the stannic chloride concentration is about 10^{-1} mole l.⁻¹, we find that for phenylacetylene and pent-1-yne concentrations < 0.5 mole l.⁻¹, the rate of reaction increased initially to a maximum value and then decreased in the normal way. As the acetylene concentration decreased below these values, this maximum rate decreased and the time taken for its development increased.

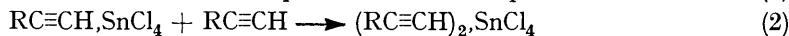
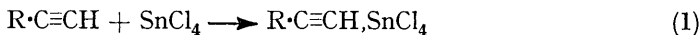
Temperature dependence. Plots of $\log_{10}R_i$ against $1/T$, at constant concentrations of stannic chloride and of the acetylenes, gave values of 12.0 ± 0.5 kcal. mole⁻¹ and 12.7 ± 0.5 kcal. mole⁻¹ for the activation energies for phenylacetylene and pent-1-yne, respectively (see Tables 5A and B). These Tables also show that the volume decrease of the reaction mixture is independent of temperature.

DISCUSSION

Mechanism of Reaction.—The mechanism proposed for these systems in which the initial acetylene concentration is at least five times as great as the initial stannic chloride concentration, must satisfy the following: (1) The reaction product contains two acetylene units complexed with one stannic chloride molecule. (2) The initial rate of reaction is of the first order in stannic chloride and in the acetylene concentration. (3) Hydrogen chloride has no effect on the initial rate of reaction, but markedly affects the colour of reaction solutions. (4) In the presence of excess of the acetylene, the extent of reaction is proportional to the stannic chloride concentration, and is independent of the temperature in the range 30–55°. (5) For a given stannic chloride concentration there is a minimum

acetylene concentration below which the reaction rate is not a maximum value initially but builds up gradually to its maximum value before decreasing in the normal way.

We postulate the following mechanism:



where R = Ph or Pr.

If reaction (1) is fast and reaction (2) slower and rate determining, then in the presence of the large excess of acetylene, all the stannic chloride will be complexed before any appreciable addition of the second molecule of the acetylene can occur. Thus:

$$\text{Initial rate} = k_2\{[\text{RC}\equiv\text{CH}]_i - [\text{SnCl}_4]_i\}[\text{RC}\equiv\text{CH},\text{SnCl}_4]$$

$$\text{But} \quad [\text{RC}\equiv\text{CH},\text{SnCl}_4]_i = [\text{SnCl}_4]_i$$

$$\text{Therefore, initial rate} = k_2\{[\text{RC}\equiv\text{CH}]_i - [\text{SnCl}_4]_i\}[\text{SnCl}_4]_i$$

Since in our systems the acetylene is always in great excess over the stannic chloride, this relation would lead to the observed first order dependence of the initial rate on stannic chloride and acetylene. Values of $R_i/\{[\text{RC}\equiv\text{CH}]_i - [\text{SnCl}_4]_i\}$ at constant $[\text{SnCl}_4]_i$ are given in Tables 3A and B. This mechanism also agrees with the fact that the extent of reaction depends on the concentration of stannic chloride.

As the concentration of the acetylene is decreased, the rates of reactions (1) and (2) will decrease. If reaction (1) slows down sufficiently, it will take an appreciable time for the concentration of complex $\text{RC}\equiv\text{CH},\text{SnCl}_4$ to reach its maximum value. This will result in an initial period during which the rate of reaction (2) will increase to a maximum before decreasing in the normal way.

The fact that the extent of reaction is independent of temperature suggests that no equilibrium is involved and that reactions (1) and (2) go to completion.

According to our mechanism the activation energies of 12.0 kcal. mole⁻¹ and 12.7 kcal. mole⁻¹ for the phenylacetylene and pent-1-yne reactions, respectively, will be those for the addition of a molecule of the acetylene to the acetylene-SnCl₄ complex, ΔH_2^\ddagger .

Reaction Products.—The phenylacetylene product has a =CH₂ group in its structure as seen by infrared spectral examination, and the original acetylene cannot be regenerated from it by treatment with water. This suggests that the stannic chloride activates a molecule of the acetylene and causes it to react with a second molecule by hydrogen migration to form a complex of the type $\text{SnCl}_4,\text{PhC}\equiv\text{C}-\text{CPh}=\text{CH}_2$. The pent-1-yne product on the other hand has no =CH₂ group and treatment with water regenerates the original acetylene.

The effect of hydrogen chloride on the colour of reacting systems suggests that a small amount of a secondary reaction is taking place. We postulate that this is a polymerisation reaction of the cationic type with stannic chloride as the Friedel-Crafts catalyst and hydrogen chloride as the co-catalyst, producing a polymer containing conjugated double bonds which would impart an intense colour to reacting solutions, even when present in small amounts. This polymerisation reaction occurs to only a very small extent.

Thus, these acetylenic compounds behave very differently in stannic chloride-hydrogen chloride systems from 1,1-diphenylethylene.⁴ The main reaction of the olefin involves the formation of a carbonium ion by proton addition. For the acetylenes, however, the main reaction is complex formation with stannic chloride, very little proton addition taking place.

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