

133. The Activation of Carbon-Carbon Double Bonds by Cationic Catalysts. Part XI.¹ The Interaction of Titanium Tetrachloride with 1,1-Diphenylethylene and Related Compounds in the Absence of a Co-catalyst.

By B. ELLIOTT, ALWYN G. EVANS, and E. D. OWEN.

In studies of systems involving 1,1-diphenylethylene, a Friedel-Crafts catalyst, and a co-catalyst, we now find that, in the absence of a co-catalyst (where no reaction can occur), there is complex-formation between titanium tetrachloride and 1,1-diphenylethylene.

Interaction of titanium tetrachloride and benzene, 1,1-diphenylethane, 1,1,3,3-tetraphenylbut-1-ene, and 1-methyl-1,3,3-triphenylindane has also been studied. In these cases, too, complexes are formed.

WE describe here experiments in which titanium tetrachloride and 1,1-diphenylethylene or related compounds are brought together in hexane. Spectroscopical examination shows complexes to be formed.

EXPERIMENTAL

Materials.—Benzene was purified as in Part V² and was left over sodium-potassium alloy for not less than 2 months before use. Hexane (B.D.H.), of spectroscopic standard, was sealed in glass ampoules over sodium-potassium alloy, techniques being analogous to those used in the purification of benzene. Titanium tetrachloride was prepared as described in Part IX,³ and 1,1-diphenylethylene by the stannic chloride treatment described in Part V.³ 1,1,3,3-Tetraphenylbut-1-ene was prepared from 1,1-diphenylethylene as described in Part VIII.⁴ 1-Methyl-1,3,3-triphenylindane was prepared by the action of stannic chloride and hydrogen chloride on 1,1-diphenylethylene, as described by Schoepfle and Ryan;⁵ it was purified by recrystallisation from isopropyl alcohol, the final product melting sharply at 143° and giving no colour with "AnalaR" concentrated sulphuric acid (showing absence of 1,1,3,3-tetraphenylbut-1-ene). 1,1-Diphenylethane was prepared from benzene and acetylene by Reichert and Nieuwland's method;⁶ it was repeatedly fractionated under reduced pressure and dried over sodium and its 1,1-diphenylethylene content determined by bursting bulbs of it beneath "AnalaR" concentrated sulphuric acid and measuring the intensity of the carbonium ion absorption. In this way the 1,1-diphenylethylene impurity was shown to be less than 0.5%.

Procedure.—The reaction of titanium tetrachloride with 1,1-diphenylethylene and related compounds was studied spectroscopically. Hexane was used as solvent since hexane solutions of titanium tetrachloride show no absorption in the visible region. However, since they do absorb in the near-ultraviolet region, the control cells were made up with a titanium chloride solution of the same composition as that of the sample investigated.

Solutions containing also benzene, 1,1-diphenylethylene (monomer), 1,1-diphenylethane (hydrogenated monomer), 1,1,3,3-tetraphenylbut-1-ene (linear dimer), or 1-methyl-1,3,3-triphenylindane (cyclic dimer), of known concentration and the corresponding controls were made up in a high-vacuum system by techniques described previously.² These solutions were then studied in a Unicam S.P. 700 spectrophotometer. The effect of temperature on the optical density of these solutions was also measured over the range 20–70°. A correction was made for the expansion of the solvent over this range.

RESULTS

Benzene.—The reaction of titanium tetrachloride with benzene gave the spectrum shown in Fig. 1, curve A. The spectrum extends into the visible region and the solutions are pale yellow. A benzene-hexane solution is colourless and does not absorb over this range. The titanium tetrachloride-hexane solution (Fig. 1, curve B) is colourless but shows a rapid increase

¹ Part X, Evans, James, and Owen, *J.*, 1961, 3532.

² Evans and Lewis, *J.*, 1957, 2975.

³ Evans and Owen, *J.*, 1959, 4123.

⁴ Evans and Price, *J.*, 1959, 2982.

⁵ Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, 52, 4021.

⁶ Reichert and Nieuwland, *J. Amer. Chem. Soc.*, 1923, 45, 3090.

in absorption above $28,500\text{ cm}^{-1}$. Because of this we have not extended the absorption diagram above $28,500\text{ cm}^{-1}$ since the spectrometer cannot deal with systems involving controls of high optical density.*

Mixing the two colourless solutions, benzene-hexane and titanium tetrachloride-hexane gives a coloured system and this shows the formation of a coloured complex between benzene and the chloride. To determine the dependence of the concentration of this complex on $[\text{Benzene}]$ and on $[\text{TiCl}_4]$, two series of solutions were made up, one having constant benzene and varying tetrachloride concentration, the other having constant tetrachloride and varying benzene concentration. The optical density at $357\text{ m}\mu$ ($28,000\text{ cm}^{-1}$) was taken as a measure of the complex concentration since at this wavelength any possible difference in the tetrachloride concentration of the sample and the control would have no effect (see Fig. 1). The results (Tables 1 and 2) show that a 1:1 complex is formed between benzene and titanium tetrachloride.

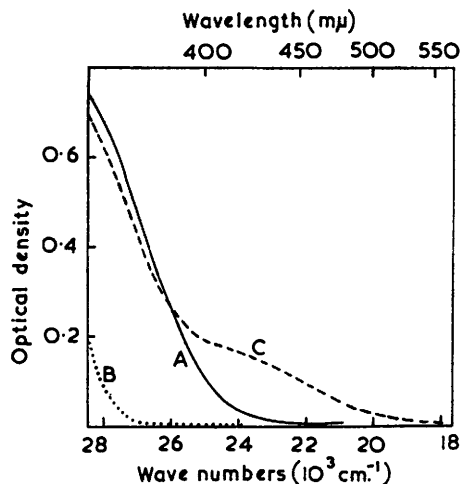


FIG. 1. Absorption spectra of hexane solutions of (A) TiCl_4 ($4.75 \times 10^{-2}\text{M}$) and C_6H_6 ($6.10 \times 10^{-2}\text{M}$), (B) TiCl_4 ($4.75 \times 10^{-2}\text{M}$), and (C) TiCl_4 ($3.58 \times 10^{-2}\text{M}$) and $\text{CH}_2:\text{CPh}_2$ ($3.00 \times 10^{-2}\text{M}$).

1,1-Diphenylethylene.—Reaction of the tetrachloride with 1,1-diphenylethylene gave a pale yellow solution having the spectrum shown in Fig. 1, curve C. The spectrum shows the formation of a complex between 1,1-diphenylethylene and the tetrachloride. The dependence of the concentration of this complex on $[\text{TiCl}_4]$ and $[\text{CH}_2:\text{CPh}_2]$ was determined as for the case of benzene and the results are given in Tables 3 and 4. It is seen that the production of the $\text{TiCl}_4\text{CH}_2:\text{CPh}_2$ complex depends on $[\text{CH}_2:\text{CPh}_2]$ to the first power but depends on $[\text{TiCl}_4]$ to a power which is less than unity. A plot of $\log_{10} [\text{TiCl}_4]$ against $\log_{10} (\text{O.D., } 357\text{ m}\mu)$ gave a straight line of slope 0.84 (Fig. 2).

Related Compounds.—Reaction of titanium tetrachloride with 1,1-diphenylethane, 1,1,3,3-tetraphenylbut-1-ene, and 1-methyl-1,3,3-triphenylindane was studied; the spectra obtained are given in Fig. 3.

TABLE 1.

Dependence of $[\text{TiCl}_4\text{C}_6\text{H}_6]$ on $[\text{C}_6\text{H}_6]$ ($[\text{TiCl}_4] = 4.75 \times 10^{-2}\text{M}$).						
$[\text{C}_6\text{H}_6]$ (10^{-2}M)	1.39	3.24	4.94	6.99	9.78	12.18
OD, 357 $\text{m}\mu$ *	0.152	0.367	0.552	0.780	1.11	1.41
OD/ $[\text{C}_6\text{H}_6]$	10.9	11.3	11.2	11.2	11.3	11.6

* OD = optical density at stated wavelength.

TABLE 2.

Dependence of $[\text{TiCl}_4\text{C}_6\text{H}_6]$ on $[\text{TiCl}_4]$ ($[\text{C}_6\text{H}_6] = 5.40 \times 10^{-2}\text{M}$).						
$[\text{TiCl}_4]$ (10^{-2}M)	1.23	2.59	3.88	5.27	6.21	9.66
OD, 357 $\text{m}\mu$	0.159	0.324	0.420	0.625	0.73	1.165
OD/ $[\text{TiCl}_4]$	12.9	12.5	10.8	11.9	11.8	12.1

* This fact was kindly pointed out to us by a Referee, and we have carried out experiments which confirm it.

TABLE 3.

Dependence of $[\text{TiCl}_4 \cdot \text{CH}_2 \cdot \text{CPh}_2]$ on $[\text{CH}_2 \cdot \text{CPh}_2]$ ($[\text{TiCl}_4] = 2.20 \times 10^{-2} \text{M}$).

$[\text{CH}_2 \cdot \text{CPh}_2] (10^{-2} \text{M})$	0.841	1.98	3.49	4.68	6.22	8.89
OD, 357 $\text{m}\mu$	0.120	0.330	0.479	0.782	0.93	1.3
OD/ $[\text{CH}_2 \cdot \text{CPh}_2]$	14.3	16.7	13.7	16.7	15.0	14.6

TABLE 4.

Dependence of $[\text{CH}_2 \cdot \text{CPh}_2 \cdot \text{TiCl}_4]$ on $[\text{TiCl}_4]$.(a) $[\text{CH}_2 \cdot \text{CPh}_2] = 3.00 \times 10^{-2} \text{M}$.

$[\text{TiCl}_4] (10^{-2} \text{M})$	1.33	2.33	3.58	5.26	8.45
OD, 357 $\text{m}\mu$	0.323	0.423	0.615	0.87	1.23
OD/ $[\text{TiCl}_4]$	24.3	18.2	17.2	16.5	14.6

(b) $[\text{CH}_2 \cdot \text{CPh}_2] = 1.98 \times 10^{-2} \text{M}$.

$[\text{TiCl}_4] (10^{-2} \text{M})$	1.37	2.20	3.38	4.94	6.69
OD, 357 $\text{m}\mu$	0.201	0.330	0.432	0.555	0.738
OD/ $[\text{TiCl}_4]$	14.7	15.0	12.8	11.2	11.0

TABLE 5.

 ΔH° values for complex formation of various reagents with TiCl_4 .

Reagent	C_6H_6	$\text{CH}_2 \cdot \text{CPh}_2$	$\text{CH}_3 \cdot \text{CHPh}_2$	$\text{CH}_3 \cdot \text{CPh}_2 \cdot \text{CH} \cdot \text{CPh}_2$	1-Methyl-1,3,3-triphenylindane
ΔH° (kcal. mole $^{-1}$) ...	-0.30	-0.36	-0.52	-0.21	-0.17

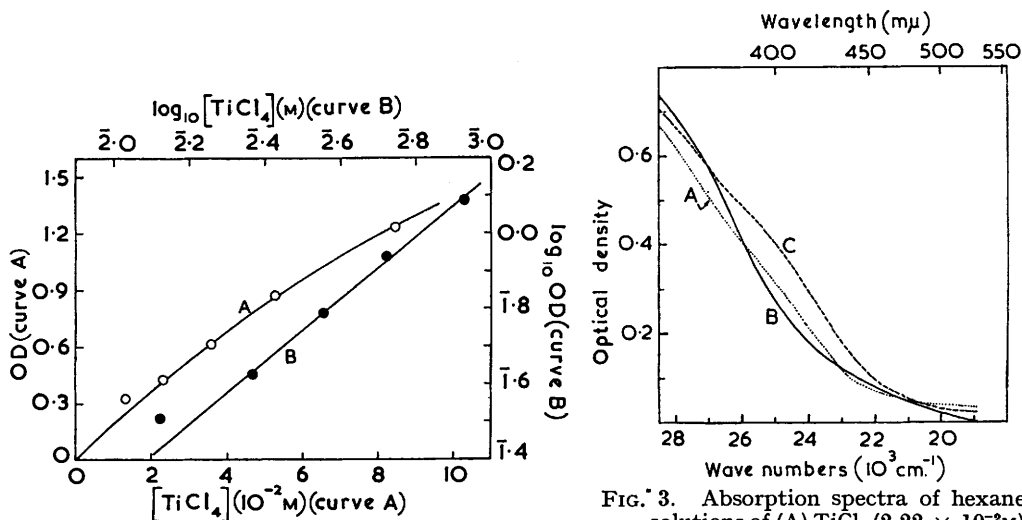


FIG. 2. Dependence of $[\text{TiCl}_4 \cdot \text{CH}_2 \cdot \text{CPh}_2]$ on $[\text{TiCl}_4]$. $[\text{CH}_2 \cdot \text{CPh}_2] = 3.00 \times 10^{-2} \text{M}$. OD = Optical density at 28,000 cm^{-1} .

FIG. 3. Absorption spectra of hexane solutions of (A) TiCl_4 ($2.22 \times 10^{-2} \text{M}$) and $[\text{CH}_3 \cdot \text{CHPh}_2]$ ($5.09 \times 10^{-2} \text{M}$), (B) TiCl_4 ($5.18 \times 10^{-2} \text{M}$) and $\text{CH}_3 \cdot \text{CPh}_2 \cdot \text{CH} \cdot \text{CPh}_2$ ($1.70 \times 10^{-2} \text{M}$), and (C) TiCl_4 ($5.18 \times 10^{-2} \text{M}$) and 1-methyl-1,3,3-triphenylindane ($1.75 \times 10^{-2} \text{M}$).

Temperature-dependence.—The effect of temperature on the optical density of these solutions enables us to obtain the ΔH° value for the formation of the coloured complex. The results are given in Table 5.

DISCUSSION

Effect of Reagent Concentration on Complex Formation.—For the reaction of titanium tetrachloride with benzene the interaction may be written $\text{TiCl}_4 + \text{C}_6\text{H}_6 \xrightleftharpoons[b]{a} \text{TiCl}_4 \cdot \text{C}_6\text{H}_6$.

Since the dependence of complex concentration on reagent concentration is to the first power, even when each reagent is in turn used in excess of the other (Tables 1 and 2), this equilibrium must lie well to the left. (Brown and Wallace⁷ have shown from vapour pressure measurements that aluminium bromide and benzene form a complex $\text{Al}_2\text{Br}_6\cdot\text{C}_6\text{H}_6$).

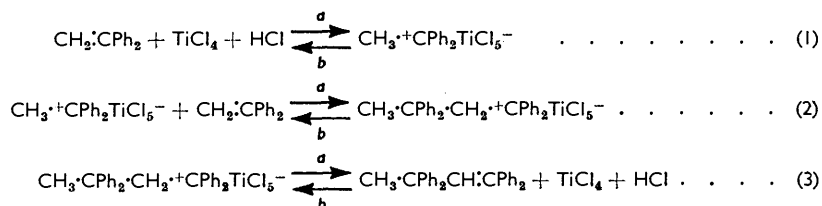
For titanium tetrachloride and 1,1-diphenylethylene, the complex concentration depends on $[\text{olefin}]^1$ and $[\text{TiCl}_4]^{0.84}$. It is difficult to understand why the power in tetrachloride is less than unity for the complex with 1,1-diphenylethylene since it is so close to unity for its complex with benzene. We feel that this is a real effect since the experiments were very carefully repeated, with the same result. One would expect a smaller power of this kind if the equilibrium were not sufficiently far to the left, but in that case one would expect also the power in 1,1-diphenylethylene to be less than unity, and this is not so. It cannot be due to any equilibrium involving dimeric chloride since the same conditions operate as in the experiments with benzene, where the order in chloride is unity.

Spectra.—That 1,1-diphenylethane and 1-methyl-1,3,3-triphenylindane give coloured complexes is strong evidence that titanium tetrachloride interacts with the phenyl groups of the olefins, 1,1-diphenylethylene and 1,1,3,3-tetraphenylbut-1-ene. In the case of 1,1-diphenylethylene, however, there is clear evidence of an unresolved band at 23,000—24,000 cm^{-1} (see Fig. 1, curve C).

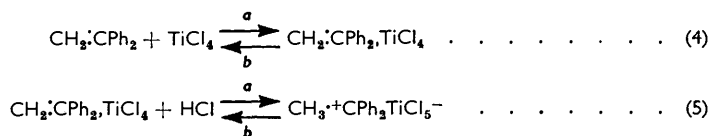
For a given concentration of reagents the optical density at 28,000 cm^{-1} is greater for 1,1-diphenylethylene and its related compounds than it is for benzene.

Temperature-dependence.—The values of ΔH° for complex formation are small (see Table 5) (between -0.2 and -0.5 kcal. mole^{-1}). The correction for volume change with temperature is of the order of 0.6 kcal. mole^{-1} , so we do not attach much importance to the small differences between these ΔH° values.

Mechanism of Dimerisation.—For the dimerisation of 1,1-diphenylethylene in benzene catalysed by titanium tetrachloride with hydrogen chloride as co-catalyst, the initial rate of reaction is of the first order in hydrogen chloride and titanium chloride and of the second order in diphenylethylene.³ We have interpreted these orders previously according to the following scheme in which reaction (2a) is the rate-determining step in the forward direction.



Our present results suggest that reaction (1) may be rewritten:



Since equilibrium (4) lies well to the left, this would lead to the same orders for the reaction as did the earlier scheme.

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CHEMISTRY DEPARTMENT, UNIVERSITY COLLEGE,
CATHAYS PARK, CARDIFF.

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⁷ Brown and Wallace, *J. Amer. Chem. Soc.*, 1953, **75**, 6265.