715. *The Cationic Oligomerisation * of the Stilbenes.*

By D. S. Brackman and P. H. Plesch.

Oligomerisation of *trans*-stilbene in benzene–hexane catalysed by titanium tetrachloride and trichloroacetic acid together is a cationic chain-reaction yielding a mixture of dimers and trimers which are substituted indanes. In toluene *trans*-stilbene gives about 50% of indane dimer and 50% of 1 : 2-diphenyl-1-*p*-tolylethane; *cis*-stilbene forms the latter almost exclusively. The rate of oligomerisation of *trans*-stilbene in benzene–hexane is of the first order in monomer and of a complex order in catalyst and co-catalyst. In *n*-hexane at 0° *cis*-stilbene gives a mixture of oligomers up to and including a pentamer: the initiating species, a complex between catalyst and co-catalyst, is involved in an equilibrium which complicates the interpretation of rate constants and activation energies.

THE scanty literature on the oligomerisation of the stilbenes contains no kinetic studies. A dimer of *trans*-stilbene was prepared photochemically[1,2] and identified as 1 : 2 : 3 : 4-tetraphenyl*cyclo*butane.[2,3] The free-radical homopolymerisation of the stilbenes has not been reported, although some copolymers have been prepared. A solution of potassium amide in liquid ammonia does not polymerise *trans*-stilbene.[4] Studies of the polymerisation of *trans*-stilbene by aluminium chloride in carbon disulphide [5,6] indicated

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* The term oligomer is used to denote low polymers, up to decamers.

[1] Ciamician and Silber, *Ber.*, 1902, **35**, 4128.

[2] Pailer and Müller, *Monatsh.*, 1948, **29**, 615.

[3] Fulton and Dunitz, *Nature*, 1947, **160**, 161.

[4] Wooding, Thesis, Leeds, 1950.

[5] Liebermann and Mitter, *Ber.*, 1912, **45**, 1212.

[6] Scholl and Schwarzer, *Ber.*, 1922, **55**, 324.

that at most a trimer was formed. Qualitative observations on the reactions of the stilbenes in the presence of boron fluoride, titanium tetrachloride, and sulphuric and trichloroacetic acid have been reported,[7] and the oligomerisations of the stilbenes in boron fluoride–ether [8] and of *trans*-stilbene in antimony trichloride [9] have also been studied. The present work deals with the oligomerisation of *cis*- and *trans*-stilbene with titanium tetrachloride as catalyst and trichloroacetic acid as co-catalyst.

EXPERIMENTAL

Materials.—Hexane and solutions of titanium tetrachloride and trichloroacetic acid in it were prepared as described earlier.[10] Spectroscopically pure *n*-hexane was prepared by treating technical hexane with fuming sulphuric acid. Benzene was purified by standard methods and stored over phosphoric oxide. Toluene was repeatedly shaken with concentrated sulphuric acid, decanted, refluxed for 1 hr. with aluminium chloride, and distilled; 75% distilled at 109—110°. The distillate was shaken with dilute aqueous sodium hydroxide and with water, dried (K_2CO_3), refluxed with sodium, and distilled through a 60 cm. Vigreux column with a reflux ratio of 10 : 1. More than 75% distilled over a range of 0·4°, and was stored over phosphoric oxide. *cis*- and *trans*-Stilbene were prepared and purified as described earlier.[7, 11]

Apparatus and Procedure.—The reaction vessel used for the isothermal experiments was a 50 ml. Pyrex flask fitted, by ground joints, with necessary inlets and a device by means of which samples of known volume could be removed from the reaction mixture at intervals for analysis, without admission of laboratory air. A weighed quantity of stilbene was introduced into the reaction vessel, the solvent (benzene) and the catalyst solution (titanium tetrachloride in hexane) were then added, and the co-catalyst solution (trichloroacetic acid in hexane) was run into a side-arm. It was necessary to use benzene as solvent since *trans*-stilbene is only very sparingly soluble in hexane. The benzene : hexane ratio varied from 2·2 to 0·77 by volume in the kinetic experiments and had no effect on the reaction rate. The vessel was kept in a thermostat-bath and when temperature equilibrium had been attained the co-catalyst and the monomer solution were mixed by tilting the vessel; samples of the reaction mixture were withdrawn at known time intervals. In the earlier experiments these samples were treated with aqueous sodium carbonate to remove catalyst and co-catalyst, the solvent was removed at about 60° under slightly reduced pressure, and unchanged monomer removed by heating the sample in a tared weighing bottle in a boiling-water bath under a high vacuum for 30 min. The quantity of oligomer left in the weighing bottle was found by weighing. With standardised technique satisfactory reproducibility was obtained. Thus the progress of the reaction with time was followed by direct weighing of the oligomer formed. In the later experiments the progress of the reaction was followed by determining the residual stilbene spectrophotometrically.

For the adiabatic experiments a stoppered Dewar vessel fitted with breakable phials, inlets, stirrer, electric heater, and a thermometer reading to 0·1° was used. The solid *trans*-stilbene and a solution of trichloroacetic acid in benzene were contained in breakable phials immersed in the solvent (benzene). The titanium tetrachloride was added as a solution in benzene. The co-catalyst phial, and subsequently the monomer phial, were broken, and the reaction thus started was followed by taking temperature readings at half-minute intervals.

Preliminary experiments showed that the oligomerisation of the stilbenes by titanium tetrachloride is fairly insensitive to traces of moisture, so that a rigorously anhydrous technique was not necessary. All reagents were handled, and the reaction mixture was kept, under dry nitrogen.

Some of the oligomers were roughly fractionated in a horizontal temperature gradient under a high vacuum. Molecular weights were determined cryoscopically in *cyclo*hexane or ebullioscopically in carbon tetrachloride. Hydrogenations were carried out in glacial acetic acid with a platinum oxide catalyst.

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[7] Brackman and Plesch, *J.*, 1953, 1289.

[8] Price and Berti, *J. Amer. Chem. Soc.*, 1954, **76**, 1219.

[9] Porter and Baughan, *J.*, 1958, 744.

[10] Plesch, *J.*, 1950, 543.

[11] Brackman and Plesch, *J.*, 1952, 2188.

RESULTS

In all the systems investigated the mixture of *trans*-stilbene and titanium tetrachloride was reddish-brown; when *cis*-stilbene was used the solutions were pale red. On addition of the trichloroacetic acid the colour did not change immediately, but faded to a pale yellow as the reaction progressed. The solutions were perfectly clear throughout, and there was no optical indication of heterogeneity, nor were deposits formed. The yield of the oligomerisations of *cis*- and *trans*-stilbene at 25° in hexane–benzene was 100% in every experiment which was allowed to go to completion. When a reaction had ceased through exhaustion of the monomer, a further portion of monomer added to the same reaction mixture, even several hours later, oligomerised readily. At temperatures above 50° the reactions did not go to completion. It was ascertained that this was not due to a monomer–oligomer equilibrium but the cause is still obscure, though there are indications that it may be due to a slow decomposition of the trichloroacetic acid.

Structure of the Oligomers.—The oligomerisation of *trans*- and *cis*-stilbene in hexane–benzene gave transparent resins, usually colourless but occasionally pale yellow, with an indefinite softening point between 50° and 80°. The molecular weights of all products were less than 1000. Since yields greater than 100% were never found, although specifically looked for, alkylation of benzene by stilbene cannot be an important reaction under the conditions of these experiments.

Theoretically, stilbene could form the following dimers without rupture of a C–C bond: (I) 1 : 2 : 3 : 4-tetraphenylbut-1-ene; (II) 1 : 2 : 3 : 4-tetraphenylbut-2-ene; (III) 1-benzyl-1 : 2-diphenylindane; (IV) 1-benzyl-2 : 3-diphenylindane; (V) 9 : 10-dihydro-9-(1 : 2-diphenylethyl)phenanthrene; (VI) 1 : 2 : 3 : 4-tetrahydro-1 : 2 : 3-triphenylnaphthalene; (VII) 1 : 2 : 3 : 4-tetraphenyl*cyclo*butane; (VIII) 4-(1 : 2-diphenylethyl)stilbene; (IX) cyclised derivatives of (VIII).

The trimers and higher members of the series would be: (*a*) Straight-chain, phenyl-substituted alk-1-enes or alk-2-enes analogous to (I) and (II); (*b*) indanes analogous to (III) and (IV) with phenylated *n*-propyl, *n*-pentyl, etc., groups in place of the benzyl group; (*c*) dihydrophenanthrenes analogous to (V), with phenylated *n*-butyl, *n*-hexyl, etc., groups in place of the phenylated ethyl group; (*d*) although no higher analogues of (VI) or (VII) are possible, macrocyclic rings could be formed, *e.g.*, by *para*-cyclisation; (*e*) higher oligomers involving structures similar to (VIII).

The oligomers produced from *trans*-stilbene in hexane–benzene were hydrocarbons [Found: C, 93·75, 93·2; H, 6·95, 6·85. $(C_{14}H_{12})_n$ requires C, 93·3; H, 6·7%]. The molecular weights were in the range 350—600 (Calc. for $C_{14}H_{12}$: *M*, 180·2). The ultraviolet spectrum showed a single strong peak near 2650 Å and, in some specimens, a low peak near 3000 Å which was removed by hydrogenation. Comparison with the spectrum of *trans*-stilbene showed that there was not more than 10 mole % of the unsaturation (which may have been due to residual *trans*-stilbene). This evidence eliminates structures (I) and (II), and also (V) which would have given an absorption resembling that of diphenyl. Structure (VII) was eliminated by comparison of the infrared spectra with that of an authentic sample obtained by courtesy of Dr. E. Bergmann. Structures (VIII) and (IX) are eliminated because the infrared spectra showed no trace of *para*-substitution. The infrared spectra of all the oligomers were similar, and almost unchanged by hydrogenation; they showed a great resemblance to that of polystyrene. One prominent feature is a strong band at 750 cm.$^{-1}$, easily distinguished from another at 760 cm.$^{-1}$, and not present in the spectrum of polystyrene. A detailed comparison with the infrared spectra of various substituted indanes and tetrahydronaphthalenes, and also chemical analogy with the formation of indane dimers from α-methylstyrene [12] and styrene,[13] all suggest that the stilbene oligomer is most probably a mixture of the dimer 1-benzyl-2 : 3-diphenylindane and of the corresponding trimer, 1 : 2-diphenyl-3-(1 : 2 : 3-triphenyl-*n*-propyl)indane. It should be noted that the dimer can exist in four geometrically isomeric forms.

Oligomerisation of *trans*-stilbene in toluene gave a product which was separated by high-vacuum distillation into two approximately equal fractions. The less volatile compound (A) consisted mainly of a dimer (Found: *M*, 390; C, 93·2; H, 7·0%) having ultraviolet and infrared spectra similar to those of the oligomer formed in hexane–benzene. The other fraction (B)

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[12] Dainton and Tomlinson, *J.*, 1953, 151.

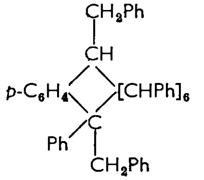
[13] Corson, Dorsky, Nickels, Kutz, and Thayer, *J. Org. Chem.*, 1954, **19**, 17.

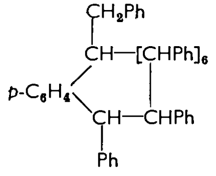
crystallised slowly; after three recrystallisations from ethanol it melted at 42—43°. It was identified by two syntheses as 1 : 2-diphenyl-1-*p*-tolylethane.[14]

Oligomerisation of *cis*-stilbene in toluene gave a single product, which was proved identical with product (B) by refractive index, m. p. and mixed m. p., and infrared spectrum.

The oligomerisation of *cis*-stilbene in *n*-hexane at 0° yielded a product which was separated by high-vacuum distillation into components (C), b. p. 150—160° (*M*, 434), and (D), b. p. 250—270° (*M*, 566), and a residue (E) (*M*, 923) (Calc. for dimer: *M*, 360; for trimer, *M*, 540; for pentamer, *M*, 900). Fraction (C) absorbed about 0·3 mol. of hydrogen, (E) absorbed none. The ultraviolet spectra of all three fractions showed no absorption above 2850 Å, indicating substantial absence of double bonds conjugated with benzene rings. The infrared spectra of fractions (C) and (D) were generally similar to those of the oligomers obtained from *trans*-stilbene in benzene. However, the spectrum of fraction (E) showed strong evidence for *para*-substitution (bands at 825, 1020, 1510, 1890 cm.$^{-1}$); in addition, there is a strong broad band near 745 cm.$^{-1}$, but the band at 760 cm.$^{-1}$ is absent, and instead there is a shoulder on the 745 cm.$^{-1}$ band indicating a strong band near 730 cm.$^{-1}$; other distinctive features of this spectrum are strong bands at 955 and 1420 cm.$^{-1}$. The whole evidence is consistent with a macrocyclic structure formed by *para*-cyclisation, such as (E.1) or (E.2).

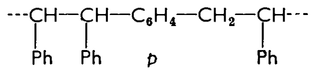
(E.1)



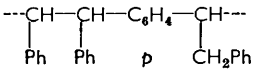


(E.2)

(E.3)



$$\cdots\underset{\mathrm{Ph}}{\mathrm{CH}}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\underset{p}{\mathrm{C_6H_4}}-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}\cdots$$



$$\cdots\underset{\mathrm{Ph}}{\mathrm{CH}}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\underset{p}{\mathrm{C_6H_4}}-\underset{\mathrm{CH_2Ph}}{\mathrm{CH}}\cdots$$

(E.4)

Another possibility is that a benzene ring is included in the chain by " perverse " propagation,[15] leading to the structures (E.3) or (E.4).

Kinetics.—trans-*Stilbene.* Adding titanium tetrachloride to a solution of *trans*-stilbene in hexane–benzene generally produced no reaction, or only a very slow one, indicating that co-catalysis by adventitious moisture was not an important effect. Adding the trichloroacetic acid solution to such a quiescent mixture induced an immediate reaction, as shown by the typical conversion–time curves in Fig. 1.

The early work (reported previously in outline [16]) indicated that a large part, in some cases up to 60%, of the reaction proceeded at nearly constant rate. However, repetition of some of these experiments with the much more sensitive spectroscopic technique indicated that the reactions were of first order with respect to monomer, suggesting that the approximate constancy of the rates found in many of the earlier experiments was an artefact. It was found later that most of the earlier experiments gave good first-order plots. In most of the experiments the oligomerisation was of the first order with respect to monomer up to more than 70%, and in some experiments to over 90%, conversion. From the logarithmic plots, examples of which are shown in Fig. 2, the first-order rate constants k_1 were obtained; as shown in Table 1, k_1 was independent of the monomer concentration. The dependence of k_1 at 25° on co-catalyst concentration is shown in Table 2 and Fig. 3, and its dependence on the catalyst concentration at 25° is shown in Table 3 and Fig. 4. The rate of oligomerisation is given by

$$-\,\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_1[\mathrm{M}] = k_2[\mathrm{M}][\mathrm{HX}]$$

where M = monomer and HX is a complex of titanium tetrachloride and trichloroacetic acid, the nature of which will be discussed below. In the earlier report,[16] it had also been stated erroneously that the rate varied as $[\mathrm{M}]^2$.

The adiabatic experiments (Table 4) carried out with very large concentrations of catalyst and co-catalyst in order to get fast reactions, also gave good first-order plots.

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[14] Brackman and Plesch, *Chem. and Ind.*, 1955, 255.

[15] Plesch, *J.*, 1953, 1662.

[16] Brackman and Plesch, in " Cationic Polymerisation and Related Complexes," Ed. P. H. Plesch, W. Heffer and Sons, Cambridge, 1953, p. 103.

The dependence of k_1 on temperature is shown in Table 5 and the activation energy in Table 7.

The oligomerisation of *trans*-stilbene in toluene gave, as mentioned above, a mixture of oligomers and of 1 : 2-diphenyl-1-*p*-tolylethane. The rate of consumption of stilbene was of first order with respect to stilbene. The kinetics of this system were not investigated in detail because it involved two simultaneous reactions.

Results obtained on the oligomerisation of *trans*-stilbene in pure *n*-hexane are shown in Table 5.

FIG. 1.

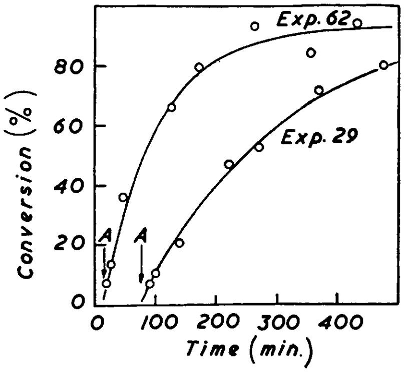

FIG. 2.

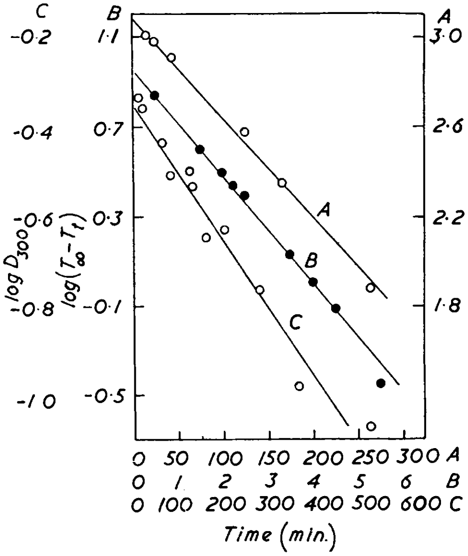

FIG. 1. *Typical time–conversion curves for the oligomerisation of* trans-*stilbene in benzene–hexane at* 25°. The titanium tetrachloride was added at time = 0, and the trichloroacetic acid at the time marked *A*.
Expt. 29: $[C_{14}H_{12}] = 0{\cdot}16$, $[TiCl_4] = 0{\cdot}082$, $[CCl_3{\cdot}CO_2H] = 0{\cdot}019$ mole/l.
$A = 72$ min. $k_1 = 6{\cdot}9 \times 10^{-5}$ sec.$^{-1}$.
Expt. 62: $[C_{14}H_{12}] = 0{\cdot}15$, $[TiCl_4] = 0{\cdot}20$, $[CCl_3{\cdot}CO_2H] = 0{\cdot}011$ mole/l.
$A = 15$ min. $k_1 = 1{\cdot}7 \times 10^{-4}$ sec.$^{-1}$.

FIG. 2. *First-order plots for the oligomerisation of* trans-*stilbene at* 25°.
A, Gravimetric: $(W_\infty - W_t)$ is the mass of monomer remaining at time *t*.
B, Adiabatic: T_t is the temperature at time *t* and T_∞ the final temperature, corrected for cooling.
C, Spectroscopic: D_{300} is the optical density at 300 mμ at time *t*, due to absorption by the *trans*-stilbene.
A: Expt. 62, see Fig. 1.
B: Expt. 134, see Table 4.
C: $[C_{14}H_{12}] = 0{\cdot}10$, $[TiCl_4] = 0{\cdot}080$, $[CCl_3{\cdot}CO_2H] = 0{\cdot}010$ mole/l.

TABLES 1—3. *Oligomerisation of* trans-*stilbene at* 25°.

(1) $[TiCl_4] = 0{\cdot}08$ mole/l. $[CCl_3{\cdot}CO_2H] = 0{\cdot}01$ mole/l.

$[C_{14}H_{12}]$ (mole/l.)	0·052	0·127	0·186	0·21	0·23	0·25	0·273
10^5k_1 (sec.$^{-1}$)	3·99	2·50	4·37	4·44	4·74	4·09	2·63

Average k_1 $3{\cdot}82 \times 10^{-5}$ sec.$^{-1}$. Standard deviation 24%.

(2) $[C_{14}H_{12}] = 0{\cdot}15$ mole/l. (*A*) $[TiCl_4] = 0{\cdot}20$ mole/l.

$10^2[CCl_3{\cdot}CO_2H]$ (mole/l.) ...	0·58	0·78	1·41	1·81	1·80	2·40	2·45	3·13
10^5k_1 (sec.$^{-1}$)	3·93	6·54	13·0	21·9	16·0	33·0	30·0	31·8

(*B*) $[TiCl_4] = 0{\cdot}084$ mole/l.

$10^2[CCl_3{\cdot}CO_2H]$ (mole/l.) ...	0·10	0·39	0·50	0·97	1·65	1·88	3·39	3·70
10^5k_1 (sec.$^{-1}$)	0·32	1·36	3·08	2·30	5·15	6·88	7·50	8·06

(3) $[C_{14}H_{12}] = 0{\cdot}15$ mole/l. $[CCl_3{\cdot}CO_2H] = 0{\cdot}012$ mole/l.

$10^2[TiCl_4]$ (mole/l.)	1·04	3·6	6·4	9·6	14·6	19·0
10^5k_1 (sec.$^{-1}$)	1·16	2·72	4·75	9·45	11·02	11·22

TABLE 4. *Adiabatic oligomerisation of* trans-*stilbene at* 20—25° *in benzene.*

Expt. no.	132	127	135	116	119	134
$[C_{14}H_{12}]$ (mole/l.)	0·153	0·294	0·300	0·367	0·432	0·452
$[TiCl_4]$ (mole/l.)	0·397	0·386	0·385	0·376	0·376	0·376
$[CCl_3{\cdot}CO_2H]$ (mole/l.)	0·063	0·061	0·061	0·091	0·060	0·060
10^3k_1 (sec.$^{-1}$)	9·10	9·46	8·89	9·64	10·15	9·38

Average $k_1 = 9{\cdot}27 \times 10^{-3}$ sec.$^{-1}$.

TABLE 5. *Oligomerisation of* trans-*stilbene.*

Exp. no.	Temp.	$[C_{14}H_{12}]$ (mole/l.)	$[TiCl_4]$ (mole/l.)	$[CCl_3{\cdot}CO_2H]$ (mole/l.)	10^5k_1 (sec.$^{-1}$)	Average 10^5k_1 (sec.$^{-1}$)	Method
			In benzene–hexane				
92	0°	0·116	0·080	0·010	3·66	2·46	Grav.
91	,,	0·125	,,	,,	1·66	—	,,
101A	,,	0·193	,,	,,	3·05	—	,,
3NA	,,	0·210	0·075	0·0094	2·31	—	Spec.
5NA	,,	0·214	,,	,,	1·62	—	,,
Table 1	25	—	0·080	0·010	3·92	3·92	Average
3NC	45	0·210	0·075	0·0094	5·72	5·98	Spec.
5NC	,,	0·214	,,	,,	6·24	—	,,
			In toluene–hexane				
33	0	0·120	0·050	0·0118	1·00	—	Grav.
25	25	0·144	0·050	0·0117	3·59	3·30	,,
65	,,	0·194	0·087	0·0097	3·01	—	,,
			In hexane				
10NA	25	0·122	0·080	0·010	1·18	—	Spec.
10NB	45	,,	,,	,,	1·70	—	,,

cis-*Stilbene.* The oligomerisations of *cis*-stilbene in hexane–benzene, pure hexane, and toluene–hexane mixtures were also of the first order with respect to monomer. The results are shown in Tables 6 and 7. These systems were not investigated in detail.

TABLE 6. *Oligomerisation of* cis-*stilbene.*

$[TiCl_4] = 0{\cdot}08$ mole/l. $[CCl_3{\cdot}CO_2H] = 0{\cdot}01$ mole/l.

No.	$[C_{14}H_{12}]$ (mole/l.)	10^5k (sec.$^{-1}$)	Average 10^5k_1 (sec.$^{-1}$)	Method	No.	$[C_{14}H_{12}]$ (mole/l.)	10^5k_1 (sec.$^{-1}$)	Average 10^5k_1 (sec.$^{-1}$)	Method
	In benzene–hexane at 0°					In benzene–hexane at 25°			
83	0·096	5·50	4·66	Grav.	79	0·109	7·47	7·16	Grav.
84	0·099	5·52	—	,,	76	0·118	9·28	—	,,
4NA	0·160	3·46	—	Spec.	4NB	0·130	5·34	—	Spec.
	In toluene–hexane at 0°					In toluene–hexane at 25°			
11NA	0·107	1·50	1·64	Spec.	11NB	0·107	3·25	3·06	Spec.
9NA	0·123	1·92	—	,,	9NB	0·123	2·09	—	,,
8NA	0·125	1·17	—	,,	8NB	0·125	2·86	—	,,
12NA	0·125	1·98	—	,,	12NB	0·125	3·97	—	,,
	In hexane					In hexane at 25°			
80	0·188 (18°)	0·0515	—	Grav.	7NB	0·128	5·88	4·91	Spec.
7NA	0·128 (0°)	1·65	—	Spec.	120	0·128	3·94	—	Grav.

TABLE 7. *Summary of kinetic results.*

cis				*trans*			
Solvent	Temp.	Average 10^5k_1 (sec.$^{-1}$)	E * (kcal. mole^{-1})	Solvent	Temp.	Average 10^5k_1 (sec.$^{-1}$)	E * (kcal. mole^{-1})
C_6H_6–C_6H_{14}	0°	2·46	3·7	C_6H_6–C_6H_{14}	0°	4·66	2·8
	25	3·92			25	7·16	
	45	5·98		PhMe–C_6H_{14}	0	1·64	4·0
PhMe–C_6H_{14}	25	3·30			25	3·06	
				C_6H_{14}	25	4·91	

* Evaluated only when more than one result at each temperature is available.

DISCUSSION

Our evidence concerning the oligomerisation of the stilbenes catalysed by titanium tetrachloride and trichloroacetic acid can be interpreted in terms of a cationic chain-reaction essentially similar to the oligomerisations and polymerisations of other olefins by similar systems. However, a detailed analysis of our results is made particularly awkward by the facts that, not only is the catalytic species produced by an equilibrium reaction between the catalyst and the co-catalyst, but the catalyst itself is undoubtedly involved in complex formation with the solvent (benzene)[17] and with the monomers.[7]

The Nature of the Initiator.—The plots in Fig. 3 show that the rate of oligomerisation of *trans*-stilbene is directly proportional to the concentration of trichloroacetic acid (AH) only when the titanium tetrachloride (C) is in considerable excess. This suggests that the initiating complex is involved in an equilibrium; four such equilibria suggest themselves:

FIG. 3.

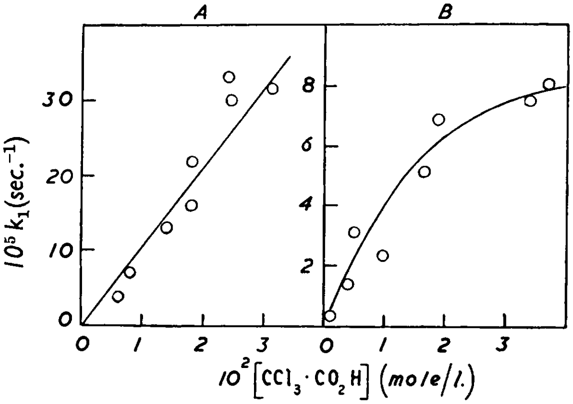

FIG. 3. *Oligomerisation of* trans-*stilbene in benzene–hexane. Dependence of first-order rate constant k_1 on concentration of trichloroacetic acid.*

Temp. 25°. Concn. of *trans*-stilbene 0·15 mole/l. Concn. of titanium tetrachloride: *A*, 0·20 mole/l.; *B*, 0·084 mole/l.

FIG. 4.

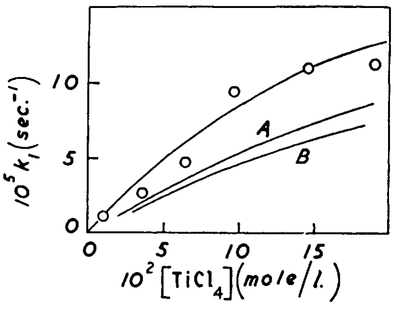

FIG. 4. *Oligomerisation of* trans-*stilbene in benzene–hexane. Dependence of first-order rate constant k_1 on concentration of titanium tetrachloride.*

Temp. 25°. Concn. of *trans*-stilbene 0·15 mole/l., concn. of trichloroacetic acid 0·012 mole/l. Line *A*, $K' = 5{\cdot}2$ l. mole^{-1}. Line *B*, $K = 0{\cdot}6$ l. mole^{-1}.

$$(\mathrm{AH})_2 + 2\mathrm{C} \rightleftharpoons 2\mathrm{C,AH} \quad K \qquad (a)$$
$$(\mathrm{AH})_2 + \mathrm{C} \rightleftharpoons \mathrm{C,(AH)_2} \quad K' \qquad (b)$$
$$(\mathrm{AH})_2 + 2\mathrm{C} \rightleftharpoons \mathrm{C_2,(AH)_2} \quad K'' \qquad (c)$$
$$(\mathrm{AH})_2 + 4\mathrm{C} \rightleftharpoons 2\mathrm{C_2,(AH)} \quad K''' \qquad (d)$$

It will be shown below that only (*a*) and (*b*) need to be considered.

Calculation of K.—If a_0 and c_0 represent the nominal concentrations of trichloroacetic acid and titanium tetrachloride in the reaction mixture, and x the concentration of C,AH, then

$$K = 2x^2/(a_0 - x)(c_0 - x)^2$$

and

$$c_0 = x + x[2/K(a_0 - x)]^{0\cdot5} \qquad (1)$$

When $c_0 \gg a_0$, virtually all the acid will be in the complex form, so that then $x = a_0$ (plot *A* of Fig. 3). We now assume that the rate of oligomerisation is given by

$-d[M]/dt = k_2[M]x$, and that for plot *A* of Fig. 3 $x = a_0$. Hence we find $k_2 = 1{\cdot}05 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. Using this value we can calculate x, and hence K, for each point on curve *B* of Fig. 3, from the relation $k_1 = k_2x$, where now $x \neq a_0$. The mean K thus obtained, $0{\cdot}51 \pm 0{\cdot}26$ l. mole^{-1}, when combined with the mean K, $0{\cdot}72 \pm 0{\cdot}17$ l. mole^{-1}, derived in a similar manner from the data of Table 1, gives a weighted mean $K = 0{\cdot}60 \pm 0{\cdot}3$ l. mole^{-1}. (The limits of uncertainty indicated here and in the following section are standard deviations.)

As a test we can calculate the curve of Fig. 4. The obvious way of doing this, to calculate x, and hence k_1, for various values of c_0, would entail the solution of a cubic equation in x; this can be circumvented by calculating x for various conveniently chosen values of k_1, and then computing the corresponding c_0 values from equation (1). The values thus obtained are shown by curve *B* in Fig. 4.

Calculation of K'.—Considering now the equilibrium (*b*) and denoting by y the concentration of the complex C,(AH)$_2$, we obtain

$$K' = 2y/(a_0 - y)(c_0 - y)$$

and

$$c_0 = 2y/K'(a_0 - y) + y \qquad \qquad (2)$$

By the same arguments as were used in the calculation of K above, we can now find a $k_2' = k_1/y = 2{\cdot}1 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$ from plot *A* of Fig. 3, assuming that for this set of experiments $y = a_0$; and then from the data of curve *B* we calculate a set of values of K'. The mean K', $4{\cdot}7 \pm 1{\cdot}7$ l. mole^{-1}, thus obtained, when combined with $K' = 5{\cdot}7 \pm 1{\cdot}3$ l. mole^{-1} obtained from the results in Table 1, gives a mean $K' = 5{\cdot}2 \pm 2$ l. mole^{-1}. Using this value, we can now calculate the k_1–c_0 curve (Fig. 4) for various conveniently chosen values of k_1; the results thus obtained for $K' = 5{\cdot}2$ l. mole^{-1} are shown in Fig. 4 (curve *A*).

Equilibria (*c*) *and* (*d*).—The appropriate computations analogous to the above show that these equilibria need not be considered.

Discrimination between Equilibria (*a*) *and* (*b*).—Neither the relative degree of constancy of K and K', nor the goodness of fit of the corresponding calculated k_1–c_0 curves in Fig. 4, affords an unambiguous discrimination between equilibria (*a*) and (*b*), though both criteria favour (*b*).

Reaction Mechanism for trans-*Stilbene in Hexane–Benzene.*—The initiation reaction most probably involves a proton-transfer from the catalytic complex to the monomer:

$$HX + C_{14}H_{12} \longrightarrow Ph{\cdot}CH_2{\cdot}{}^{+}CHPh\ X^-$$

where HX represents the catalytic complex, x = C,AH or y = C,(AH)$_2$: the resulting carbonium ion and complex anion must be associated as an ion-pair, in view of the very low dielectric constant of the solvent.

In the propagation step, the stilbene ion thus formed adds on to a stilbene molecule

$$Ph{\cdot}CH_2{\cdot}{}^{+}CHPh + C_{14}H_{12} \longrightarrow Ph{\cdot}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}{}^{+}CHPh$$

The fading of the brown-red colour of the solutions during the reaction indicates that the product does not contain double-bonds conjugated with a benzene ring; for, if it did, these would form coloured carbonium ions in the presence of the catalyst and co-catalyst and the colour of the solution would not change appreciably during the reaction. Moreover, the low molecular weight of the products indicates that chain transfer is a dominant reaction. Thus, after the first propagation step, two reaction paths are open to the " distilbene " ion: either it adds to another monomer molecule, or it undergoes cyclisation to a substituted indane by an intramolecular Friedel–Crafts reaction. The " tristilbene " ions only react by the second path, since the reaction products generally did not contain tetramers.

The indane-formation and proton-transfer reactions are probably closely associated because the indane is protonated when first formed, and then becomes " deactivated " by transferring the proton to a monomer molecule.

The fading of the colour of the reaction mixture during the reaction also shows that the carbonium ions disappear, which may indicate a regeneration of the catalytic complex:

$$\mathrm{H{\cdot}[C_{14}H_{12}]_{\mathit{n}}^{+}\,X^{-}} \longrightarrow \mathrm{[C_{14}H_{12}]_{\mathit{n}} + HX}$$

where $n = 2$ or 3. These elementary reactions can be summarised in the following scheme which is similar to that of Dainton and Tomlinson:[12]

$$\begin{array}{lrlll}
\begin{array}{l}\\ \text{or}\end{array} & \multicolumn{2}{r}{\left.\begin{array}{r}2\mathrm{C} + (\mathrm{AH})_2 \rightleftharpoons \mathrm{C,AH} \;= \\ \mathrm{C} + (\mathrm{AH})_2 \rightleftharpoons \mathrm{C,(AH)_2} = \end{array}\right\}\mathrm{HX}} & \begin{array}{l}K \;\ldots\ldots \\ K' \;\ldots\ldots\end{array} & \begin{array}{r}(\mathrm{i}a)\\ (\mathrm{i}b)\end{array}\\
& \mathrm{HX + M} \longrightarrow & \mathrm{HM^{+}X^{-}} & k_{\mathrm{i}} \;\ldots\ldots & (\mathrm{ii})\\
& \mathrm{HM^{+}X^{-} + M} \longrightarrow & \mathrm{HM_2{}^{+}X^{-}} & k_{\mathrm{p1}} \;\ldots\ldots & (\mathrm{iii})\\
& \mathrm{HM_2{}^{+}X^{-} + M} \longrightarrow & \mathrm{HM_3{}^{+}X^{-}} & k_{\mathrm{p2}} \;\ldots\ldots & (\mathrm{iv})\\
& \mathrm{HM_2{}^{+}X^{-} + M} \longrightarrow & \mathrm{M_2 + HM^{+}X^{-}} & k_{\mathrm{m2}} \;\ldots\ldots & (\mathrm{v})\\
& \mathrm{HM_3{}^{+}X^{-} + M} \longrightarrow & \mathrm{M_3 + HM^{+}X^{-}} & k_{\mathrm{m3}} \;\ldots\ldots & (\mathrm{vi})\\
& \mathrm{HM_2{}^{+}X^{-}} \longrightarrow & \mathrm{M_2 + HX} & k_{\mathrm{t2}} \;\ldots\ldots & (\mathrm{vii})\\
& \mathrm{HM_3{}^{+}X^{-}} \longrightarrow & \mathrm{M_3 + HX} & k_{\mathrm{t3}} \;\ldots\ldots & (\mathrm{viii})
\end{array}$$

If it be assumed that (*a*) the formation of complexes by titanium tetrachloride with benzene[17] and with *trans*-stilbene[7] does not affect the rate of reaction, (*b*) reactions (v) and (vi) do not affect the rate of reaction, and (*c*) the stationary state hypothesis is applicable in the form:

$$\mathrm{d[HM^{+}X^{-}]/d}t = \mathrm{d[HM_2{}^{+}X^{-}]/d}t = \mathrm{d[HM_3{}^{+}X^{-}]/d}t = 0$$

it follows that

$$-\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_{\mathrm{i}}[\mathrm{M}][\mathrm{HX}]\left[2 + \frac{k_{\mathrm{p2}}[\mathrm{M}]}{k_{\mathrm{p2}}[\mathrm{M}] + k_{\mathrm{t2}}}\right]$$

This agrees with the experimental rate law

$$-\mathrm{d[M]/d}t = k_2[\mathrm{M}][\mathrm{HX}] \quad \ldots\ldots\ldots \quad (3)$$

if $k_{\mathrm{p2}}[\mathrm{M}] \approx k_{\mathrm{t2}}$, which is not unreasonable. It follows that $k_{\mathrm{i}} = k_2/2{\cdot}5 = 4{\cdot}2 \times 10^{-3}$ l. mole^{-1} sec.$^{-1}$ at 25°. It should be noted, however, that other reaction schemes could account for the observed rate law, and these would lead to different interpretations of k_2.

If the rate of reaction is given by

$$-\mathrm{d[M]/d}t = 2{\cdot}5\; k_{\mathrm{i}}[\mathrm{M}][\mathrm{HX}]$$

and [HX] is given either by x of eqn. (1) or by y of eqn. (2), the activation energy $E = \mathrm{f}(E_{\mathrm{i}}, \Delta H)$, where E_{i} is the activation energy of reaction (ii) and ΔH the heat of reaction (*a*) or (*b*) on p. 3569; thus f cannot be evaluated in any useful manner and E cannot be interpreted explicitly.

The question arises why no high polymers are formed in this reaction. The reason is not thermodynamic, because polystilbenes of high molecular weight can be made at ambient temperatures by polymerisation of phenyldiazomethane; moreover, models confirm that steric hindrance is not excessive. The reason must therefore be kinetic, *i.e.*, after formation of the trimer the cyclisation reaction becomes very much faster than the propagation.

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[17] Cullinane, Chard, and Leyshon, *J.*, 1952, 4106.

Adiabatic Experiments.—The experiments recorded in Table 4 indicate that the rate law (3) does not apply when relatively large concentrations of catalyst and co-catalyst are used; this is particularly evident from a comparison of expt. 116 with the others: a 50% increase in the concentration of co-catalyst did not alter k_1. Moreover, if we applied this same rate law and took as an approximation [HX] = [$CCl_3 \cdot CO_2H$], k_2 would be of the order of 0·15 l. mole^{-1} sec.$^{-1}$, *i.e.*, about fifteen times as great as the k_2, or seven times the k_2' derived from the isothermal experiments. In view of the complexity of the system we cannot offer a plausible explanation for this phenomenon.

Oligomerisation of cis-*Stilbene in Benzene–Hexane.*—For the oligomerisation of *cis*-stilbene the first-order rate constant k_1 is greater, and the experimental activation energy E is smaller, than for *trans*-stilbene (Table 7). It follows from our kinetic analyses that the difference between the experimental activation energies for the oligomerisation of the two isomers, $E^c - E^t = \Delta E = -0{\cdot}9$ kcal., is equal to ΔE_i, the difference between the activation energies of the initiation reactions. ΔE_i can be correlated with the difference between the resonance energies, ΔE_{Res}, of the isomers (—4·7 kcal.), as in Fig. 5. This shows that for the addition of a proton to the double bond the difference between the resonance energies of the transition states, $\Delta E_{Res}{}^{\ddagger}$, is equal to $\Delta E_{Res} - \Delta E_i = -3{\cdot}8$ kcal. $\Delta E_{Res}{}^{\ddagger}$ is smaller than ΔE_{Res} because for *cis*-stilbene in the proton-addition transition state the steric inhibition of resonance is smaller than in the initial state.

If $A_i{}^c$ and $A_i{}^t$ are the Arrhenius pre-exponential factors of the initiation reaction for the *cis*- and the *trans*-isomers

$$\log (A_i{}^c/A_i{}^t) = \log (k_1{}^c/k_1{}^t) + \Delta E/\boldsymbol{R}\boldsymbol{T}$$

From the data of Table 7 we find that $A_i{}^c/A_i{}^t = 10$ at 0° and 8·4 at 25°, indicating that the *cis*-isomer is more accessible for proton addition than the *trans*-isomer. Thus, the greater reaction rates obtained with *cis*-stilbene are at least partly due to both a higher A factor and a lower activation energy in the initiation.

Oligomerisation of trans- *and* cis-*Stilbene in Toluene.*—The alkylation concurrent with the oligomerisation, which produces the 1 : 2-diphenyl-1-*p*-tolylethane, is closely analogous to the alkylation of toluene by the polystyrene ion, discovered by Plesch [18] and investigated by Endres and Overberger [19] and by Higashimura and Okamura.[20]

The fact that *trans*-stilbene yields about 50% of oligomer and 50% of 1 : 2-diphenyl-1-*p*-tolylethane, whereas *cis*-stilbene gives the latter exclusively, indicates that reactivity towards the stilbene cation is steeply graded in the order *trans*-stilbene > toluene > *cis*-stilbene. From our results we can estimate that the rate of reaction of a stilbene ion with *trans*-stilbene is at least a hundred times as great as the rate of its reaction with *cis*-stilbene. If we assume that for these two propagation reactions the ratio of the A factors, $A_p{}^c/A_p{}^t$, is the same as for the initiation, we find that the activation energy, E_p, of this propagation reaction is about 4 kcal. greater for *cis*- than for *trans*-stilbene. Overberger's suggestion [21] that this is due to the steric inhibition of resonance in the transition state for *cis*-stilbene is certainly valid, but is insufficient to account for the fact, illustrated in Fig. 6, that on our present hypothesis the transition state for carbonium-ion addition would lie at a level which is about 9 kcal., *i.e.*, ($\Delta E_{Res} + \Delta E_p$), higher for *cis*- than for *trans*-stilbene. This difference is almost twice as great as ΔE_{Res}; it may be symptomatic of differences in the transition states derived from the two isomers involving the stabilisation (positive or negative) of the carbonium ion, or the Coulombic energy arising from interaction with the anion X^-.

Oligomerisation of trans- *and* cis-*Stilbene in* n-*Hexane.*—The oligomerisation of both isomers in hexane is significantly slower than in solvents containing benzene or toluene.

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[18] Plesch, *J.*, 1953, 1659.

[19] Endres and Overberger, *J. Amer. Chem. Soc.*, 1955, **77**, 2201; *J. Polymer Sci.*, 1955, **16**, 283.

[20] Higashimura and Okamura, *J. High-Polymer Chem.* (*Japan*), 1956, **13**, 397.

[21] Overberger, ref. 16, p. 105.

The small difference in the dielectric constants cannot account for this difference between aliphatic and aromatic solvents which is by no means unique. Probably it is attributable to the much higher polarisability of the aromatic solvents in virtue of which solvation of polar species, in particular the transition-state complex, is much stronger, and consequently the activation energy smaller, than in aliphatic solvents. The ion-pairs will be surrounded (solvated) by the most polar or polarisable molecules available, and in hexane solution this is the monomer; thus the formation from *cis*-stilbene of oligomers up to pentamer in hexane at 0°, but not in benzene–hexane, is understandable.

Conclusion.—In the field of cationic polymerisation the isomeric stilbenes provide an opportunity for comparative structural and kinetic studies, and are worthy of further investigation. The dual catalytic system chosen by us many years ago when this work was started is not very suitable for kinetic work because of its intrinsic complexity, but the salt-like catalysts recently described [22] should prove useful also in this field.

FIG. 5.

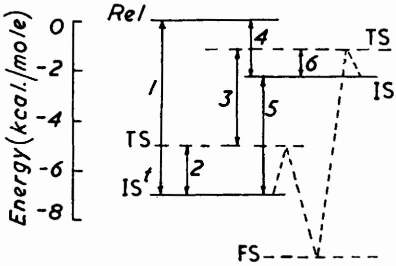

FIG. 6.

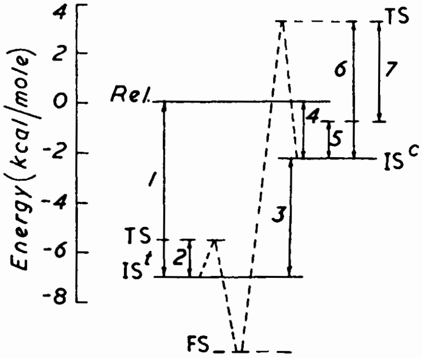

FIG. 5. *Energy-level diagram for the initiation reaction.*

The reference energy level represents the energy of the hypothetical stilbene molecule devoid of resonance interaction between the benzene rings and the double bond, plus the energy of the initiating complex HX. The energy levels shown by broken lines are indeterminate. The sloping broken lines indicate the reaction path.

REL = Reference energy level. TS = Transition state.
IS^t = Initial state, *trans*-$C_{14}H_{12}$ + HX.
IS^c = Initial state, *cis*-$C_{14}H_{12}$ + HX.
FS = Final state, $C_{14}H_{13}^+X^-$.

1, $E^t_{Res} = 7{\cdot}0$. 2, E^t_i. 3, $\Delta E_{Res}^\ddagger$. 4, $E^c_{Res} = 2{\cdot}3$. 5, $\Delta E_{Res} = 4{\cdot}7$. 6, $E^c_i = E^t_i - 0{\cdot}9$. (All units kcal./mole.)

FIG. 6. *Energy-level diagram for the propagation reaction.*

The reference energy level has the same significance as in Fig. 5 but with the stilbene ion $C_{14}H_{13}^+$ in place of HX. The significance of the broken lines is the same as in Fig. 5.

REL = Reference energy level. TS = Transition state.
IS^t = Initial state, *trans*-$C_{14}H_{12}$ + $C_{14}H_{13}^+$.
IS^c = Initial state, *cis*-$C_{14}H_{12}$ + $C_{14}H_{13}^+$.
FS = Final state, $C_{28}H_{25}^+$.

1, $E^t_{Res} = 7{\cdot}0$. 2 and 5, E^t_p. 3, $\Delta E_{Res} = 4{\cdot}7$. 4, $E^c_{Res} = 2{\cdot}3$. 6, E^c_p. 7, $\Delta E_p = 4$. (All units are kcal./mole.)

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MANCHESTER UNIVERSITY.
UNIVERSITY COLLEGE OF NORTH STAFFORDSHIRE,
KEELE, STAFFORDSHIRE.

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[22] Longworth and Plesch, *Proc. Chem. Soc.*, 1958, 117.