402. *The Activation of Carbon–Carbon Double Bonds by Cationic Catalysts. Part IV.*[1] *The Iodine-catalysed Dimerisation of* 1 : 1-*Diphenylethylene.*

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The kinetics of the reversible iodine-catalysed dimerisation of 1 : 1-diphenylethylene in 2-nitropropane to its dimer 1 : 1 : 3 : 3-tetraphenylbut-1-ene have been studied dilatometrically. The effect of the reagent concentrations on the reaction rates, and the forward and reverse activation energies have been measured. A mechanism for the dimerisation is proposed.

At low iodine concentrations the reaction does not reach true equilibrium, indicating that the catalyst is converted into some unreactive form, which, it is suggested, may be a π-complex between the iodine and the olefin.

In Parts I and II of this series[1] we investigated dilatometrically the reversible dimerisations, catalysed by trichloroacetic acid, of several 1 : 1-diarylethylenes (M) to the corresponding dimers (1 : 1 : 3 : 3-tetra-arylbut-1-enes) (D), and concluded that the reaction mechanism was :

$$x\mathrm{AH} + \mathrm{M} \underset{b}{\overset{a}{\rightleftharpoons}} (\mathrm{HM^+A^-})_{\text{solv.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

$$(\mathrm{HM^+A^-})_{\text{solv.}} + \mathrm{M} \underset{b}{\overset{a}{\rightleftharpoons}} (\mathrm{HD^+A^-})_{\text{solv.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

$$(\mathrm{HD^+A^-})_{\text{solv.}} \underset{b}{\overset{a}{\rightleftharpoons}} \mathrm{D} + x\mathrm{AH} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

where, in benzene solution, x is 3, and the solvation shell of the carbonium ion intermediates includes two molecules of dimeric trichloroacetic acid (AH).

The equilibrium (i) was confirmed by spectrophotometry (Parts II and III[1]) for the 1 : 1-di-*p*-methoxyphenylethylene–trichloroacetic acid–benzene system, and the carbonium ion was shown to be the reactive intermediate in the dimerisation.

It has been shown by Hildebrand[2] that iodine changes 1 : 1-diphenylethylene to a solid dimer, which with iodine in warm acetic acid gives back some of the monomeric olefin. The solid dimer was later shown to be 1 : 1 : 3 : 3-tetraphenylbut-1-ene.[3]

In this paper we present the results of our dilatometric studies on the iodine-catalysed dimerisation of 1 : 1-diphenylethylene in 2-nitropropane.

EXPERIMENTAL

Materials.—1 : 1-Diphenylethylene and benzene were purified as outlined in Part I,[1a] and 1-methyl-1 : 3 : 3-triphenylindane as in Part III.[1c]

1 : 1 : 3 : 3-Tetraphenylbut-1-ene was prepared either as in Part I or by treating a benzene solution of 1 : 1-diphenylethylene with iodine. In the latter method the solution was shaken after 7 days with excess of sodium thiosulphate solution to remove the iodine, and the organic layer washed with water. The benzene was distilled off, and the resultant solid washed with methanol. The solid material from both preparations was recrystallised from light petroleum (b. p. 60—80°) and fused under a high vacuum. The product was recrystallised twice from dry light petroleum (b. p. 60—80°) and had m. p. 112—113°. This showed it to be 1 : 1 : 3 : 3-tetraphenylbut-1-ene.[3]

Iodine was " AnalaR " material. It was purified either by sublimation under a high vacuum, or by recrystallisation from dry benzene. The method of purification did not affect the results.

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[1] (*a*) Part I, Evans, N. Jones, and Thomas, *J.*, 1955, 1824; (*b*) Part II, Evans, N. Jones, P. M. S. Jones, and Thomas, *J.*, 1956, 2757; (*c*) Part III, Evans, P. M. S. Jones, and Thomas, *J.*, 1957, 104.

[2] Hildebrand, Diss., Strassburg, 1909.

[3] Lebedev, Andreewsky, and Matynsekina, *Ber.*, 1923, **56**, 2350.

2-Nitropropane (from Messrs. Light) was kept over phosphoric oxide for 24 hr., then distilled off under reduced pressure and fractionated twice up a 40 cm. Vigreux column, the middle fraction, b. p. 120°, being retained (lit.,[4] b. p. 120°).

The nitrobenzene, *m*-nitrotoluene, ethylene dichloride, and *n*-hexane were all purified in the same way. They were kept over phosphoric oxide for 24 hr., then fractionated. The middle fraction was retained and refractionated. In the case of ethylene dichloride a further fractionation off anhydrous potassium carbonate was used to remove any hydrogen chloride. The middle fraction was retained in each case, the b. p.s being: nitrobenzene, 210—211° (lit.,[5] b. p. 210·8°); *m*-nitrotoluene, 230—232° (lit.,[6] b. p. 232·6°); ethylene dichloride, 83—84° (lit.,[7] b. p. 83·5°); *n*-hexane, 68—69° (lit.,[5] b. p. 68·8°).

Procedure.—The iodine was weighed directly and made up to a known concentration in the solvent. A suitable known volume was pipetted into a 100 ml. flask containing a weighed amount of monomer or dimer in solution. The mixture was made to the mark with the solvent, and the solution shaken.

The dilatometers were filled and the volumes of the solutions followed with time in thermostat baths at 54·6°, 45·9°, and 33·8°, as outlined in Part I.

The solutions were analysed when all the volume change had ceased, by shaking the contents of the dilatometers with a known excess of sodium thiosulphate solution. The iodine in the solution was then estimated by back-titration with iodine solution. The organic layer was separated off, washed with water, and evaporated to dryness under a high vacuum. The residual oily solid was washed with absolute methanol to remove residual monomer (the dimer is not very soluble in this medium). The product thus obtained was weighed, and its m. p. recorded.

n-Hexane solutions containing known concentrations of 1 : 1 : 3 : 3-tetraphenylbut-1-ene, 1-methyl-1 : 3 : 3-triphenylindane, reaction product, and mixtures of both dimers were examined spectrophotometrically with a Unicam SP500 spectrophotometer and 1 cm. silica optical cells.

RESULTS

Iodine-catalysed Dimerisation in 2-Nitropropane.—(a) *Nature of reaction products.* Solutions of iodine, 1 : 1-diphenylethylene, 1 : 1 : 3 : 3-tetraphenylbut-1-ene, or 1-methyl-1 : 3 : 3-triphenylindane, separately in 2-nitropropane, showed no volume change at 54·6° during 9 months. The unchanged materials were recovered completely after this time.

Density measurements on solutions of 1 : 1-diphenylethylene and 1 : 1 : 3 : 3-tetraphenylbut-1-ene separately in 2-nitropropane (as in Part I) show that the volume changes accompanying the complete conversion of 1 mole of monomer into 0·5 mole of but-1-ene in 1 l. of solution are 12·40 ml. at 33·8°, 12·41 ml. at 45·9°, and 12·75 ml. at 54·6°.

Mixed solutions of 1 : 1-diphenylethylene and iodine in 2-nitropropane give a volume decrease (Fig. 1, curve *A*), while those containing 1 : 1 : 3 : 3-tetraphenylbut-1-ene and iodine in 2-nitropropane give a volume increase (Fig. 1, curve *B*). Both sets of solutions reach a steady unchanging volume after some time, and analysis of such solutions gives a 100 ± 3% recovery of the iodine, together with weight of solid butene equal to within 5% of that expected from the volume change.

The crude dimer isolated from the solutions had, when washed with methanol, a m. p. within the range 106—112°; this rose after one recrystallisation from light petroleum (b. p. 60—80°) to 112—113°, showing the product to be 1 : 1 : 3 : 3-tetraphenylbut-1-ene.[3]

In view of the low m. p. of some of the samples of dimer isolated it was thought possible that traces of 3-methyl-1 : 3 : 3-triphenylindane might be formed. Solutions of the indane and butene in *n*-hexane had absorption peaks at 264 and 255 mμ respectively, and both obeyed Beer's law (ε_{264} for 1-methyl-1 : 3 : 3-triphenylindane is $1{\cdot}30 \times 10^3$; ε_{255} for 1 : 1 : 3 : 3-tetraphenylbut-1-ene is $1{\cdot}14 \times 10^4$). No indane could be detected from the absorption spectra of solutions of the crude product in *n*-hexane. (This absorption method would show the presence of indane if more than 3% were present.) A dilatometric run using a 2-nitropropane

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[4] "International Critical Tables," McGraw Hill Book Co., Inc., New York, 1929, Vol. III, p. 180.

[5] Timmermans, "Physical Chemical Constants of Pure Organic Liquids," Elsevier, Amsterdam, 1950.

[6] De Beule, *Bull. Soc. chim. belges*, 1933, **55**, 3633.

[7] Coulson, Hales, and Herington, *Trans. Faraday Soc.*, 1948, **44**, 636.

FIG. 1. *Volume–time curves for the iodine-catalysed dimerisation in 2-nitropropane.*

A, Dimerisation reaction: *initial* 1 : 1-*diphenylethylene concn.* 0·550 *mole l.*$^{-1}$; *initial iodine concn.* 7·15 × 10^{-2} *mole l.*$^{-1}$; *initial vol. of solution* 29·9 *ml.*; *temp.* 33·8°.

B, Reverse reaction: *initial* 1 : 1 : 3 : 3-*tetraphenylbut*-1-*ene concn.* 0·136 *mole l.*$^{-1}$; *initial iodine concn.* 7·1 × 10^{-2} *mole l.*$^{-1}$; *initial vol. of solution* 26·8 *ml.*; *temp.* 54·6°.

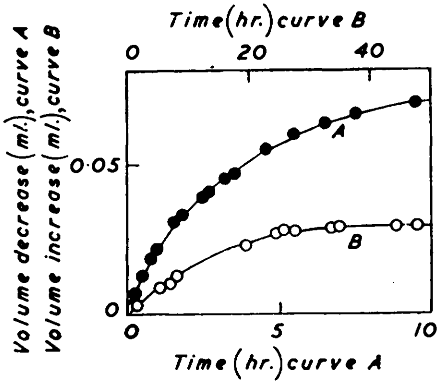
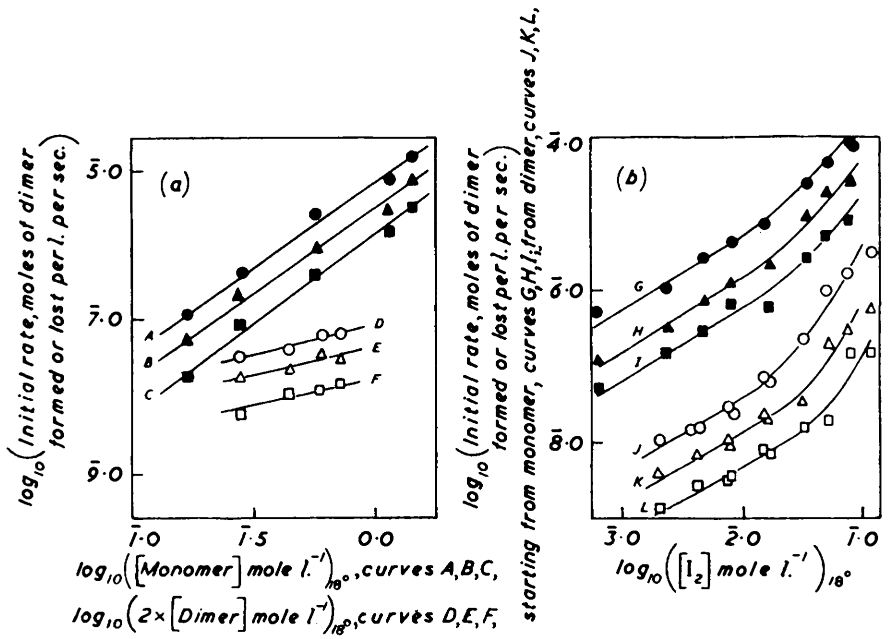


FIG. 2. *Dependence of initial rate on concentrations of monomer, dimer, and iodine.*



(*a*) *Variation of rate with olefin concn.*

Curve	Temp.	Initial I_2 concn. (10^{-2} mole l.$^{-1}$)	Slope
A	54·6°	1·50	2·0 ± 0·2
B	45·9	1·52	2·0 ± 0·2
C	33·8	1·54	2·0 ± 0·2
D	54·6	1·50	0·9 ± 0·2
E	45·9	1·52	0·95 ± 0·2
F	33·8	1·54	0·9 ± 0·2

(Curve *B* has been lowered vertically by 0·2, and curve *C* by 0·4.)

(*b*) *Variation of rate with iodine concn.*

Curve	Temp.	Initial monomer concn. (mole l.$^{-1}$)	Curve	Temp.	Initial dimer concn. (mole l.$^{-1}$)
G	54·6°	0·540	*J*	54·6°	0·285
H	45·9	0·545	*K*	45·9	0·288
I	33·8	0·550	*L*	33·8	0·291

(Curve *G* has been raised vertically by 0·5, curve *H* raised by 0·2, curve *K* lowered vertically by 0·3, and curve *L* lowered by 0·2.)

solution of iodine ($5{\cdot}5 \times 10^{-2}$ mole l.$^{-1}$), and saturated with respect to 1-methyl-1 : 3 : 3-triphenylindane ($5{\cdot}8 \times 10^{-2}$ mole l.$^{-1}$), gave no volume change at 54·6° during 5 months, at the end of which both materials were completely recovered. Any formation of indane, under the conditions of our experiments, would therefore be irreversible, and all the olefin would in time be converted into indane. Since the dimer even after several months at equilibrium always contained more than 97% of 1 : 1 : 3 : 3-tetraphenylbut-1-ene, no indane can be formed in the reaction.

Since the amounts of dimer recovered from the reaction mixtures agree closely with the amounts expected from the volume change, we may take these volume changes as giving an accurate measure of the extent of conversion of monomer into dimer or *vice versa*. Any volume changes accompanying olefin–iodine interaction must therefore be small compared with the volume changes on dimerisation. This is to be expected since the olefin was always in excess over the iodine in the reacting solutions; the ratio [1 : 1-diphenylethylene] : [iodine] varying from 6 to 10^3 for the forward reaction in 2-nitropropane, and the ratio [1 : 1 : 3 : 3-tetraphenylbut-1-ene] : [iodine] varying from 2·8 to 10^2 for the reverse reactions.

(b) *Initial rates of reaction.* The volume–time curves (of type shown in Fig. 1) were analysed by the method of initial slopes as in Part I, and the initial rates converted into moles of dimer formed or lost per l. per sec. by using the volume changes for complete reaction found from the density measurements (above).

The initial rate of the reaction and the total volume change were not affected by light, or by the surface area of the dilatometer. This was shown by comparing three solutions of the same initial monomer and iodine concentrations in 2-nitropropane, one in an ordinary dilatometer bulb, one in a bulb surrounded by tinfoil to exclude light, and one in a bulb packed with glass chips to give a large surface area. Degassing the solutions and sealing off under high vacuum had no effect on the reaction.

(c) *Dependence of the initial rate on the olefin concentration.* The initial rates were measured for a series of solutions having the same initial iodine concentration and varying initial monomer or dimer concentration. Plots were made of $\log_{10}$ (initial rate) against $\log_{10}$ [initial monomer] (Fig. 2*a*, curves *A*, *B*, *C*), or against $\log_{10}$ [initial dimer] (Fig. 2*a*, curves *D*, *E*, *F*), both at constant initial iodine concentration. These plots were straight lines the slopes of which give the orders in monomer and dimer as $2{\cdot}0 \pm 0{\cdot}2$ and $0{\cdot}9 \pm 0{\cdot}2$ respectively, at all three thermostat temperatures.

(d) *Dependence of the initial rate on iodine concentration.* The initial rates were measured similarly for a series of solutions of constant initial 1 : 1-diphenylethylene or 1 : 1 : 3 : 3-tetraphenylbut-1-ene concentration and varying initial iodine concentration. Plots were made of $\log_{10}$ (initial rate) against $\log_{10}$ [initial iodine] at constant initial monomer concentration (Fig. 2*b*, curves *G*, *H*, *I*) or constant initial dimer concentration (Fig. 2*b*, curves *J*, *K*, *L*). These were curves, showing that the order of the reaction in terms of total iodine concentration increases (0·8 to 2·1) as the iodine concentration increases over the range of concentrations used (6×10^{-4} to 10^{-1} mol. l.$^{-1}$). It is seen that the order in iodine does not vary with temperature and that for a given iodine concentration it is practically the same for both the forward and the reverse reaction. The parallelism of the two sets of curves is excellent for the two lower temperatures.

(e) *Rate constants.* In view of the changing iodine order the rate constants will be defined by equations of the type:

$$\begin{aligned}\text{Initial forward rate} &= k_f[\mathrm{M}]^2[\mathrm{I}_2]_t^{\,x}\\ \text{Initial reverse rate} &= k_r[\mathrm{D}][\mathrm{I}_2]_t^{\,x}\end{aligned}$$

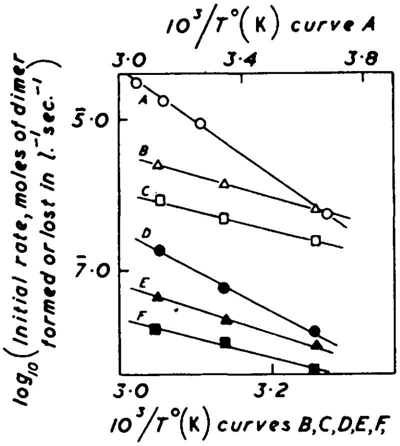
where forward rate refers to the dimerisation reaction, [M] is the monomer concentration, [D] the dimer concentration, $[\mathrm{I}_2]_t$ is the total iodine concentration, and k_f and k_r are the forward and reverse rate constants respectively, and x is the iodine order appropriate for the particular iodine concentration used. (As the two sets of curves in Fig. 2*b* are parallel, x will be the same for both forward and reverse reaction at any given iodine concentration.) We give values of of k_f and k_r for systems in which x is $1 \pm 0{\cdot}15$ (*i.e.*, where $[\mathrm{I}_2]_t$ is between 2×10^{-3} and 2×10^{-2} mole l.$^{-1}$) in Table 1.

(f) *Forward and reverse activation energies.* These have been found by measuring the initial rates of the forward and the reverse reaction at 33·8°, 45·9°, and 54·6°, for several series of solutions having constant initial iodine and olefin concentrations at room temperature.

The activation energies are then found from plots of $\log_{10}$ (initial rate) against $1/T°$ K, as shown in Fig. 3, after correcting for the small change in reagent concentrations due to thermal expansion, as in Part I.

Over the range of unit iodine order the activation energies are constant and have the values $E_f = 12{\cdot}3 \pm 0{\cdot}7$ kcal. mole^{-1} for the forward reaction, and $E_r = 19{\cdot}4 \pm 0{\cdot}8$ kcal. mole^{-1} for the reverse reaction. Both are independent of the olefin and iodine concentrations.

FIG. 3. *Activation energies for the forward and reverse reactions.*



All concns. in mole l.$^{-1}$.

Curve	[Initial monomer]$_{18°}$	[Total iodine]$_{18°}$	Iodine order x	E_f (kcal. mole^{-1})
A	0·565	0·073	1·9	14·5
B	0·565	0·0157	1·1	12·6
C	0·565	0·00465	1·0	12·3
	[Initial dimer]$_{18°}$			E_r (kcal. mole^{-1})
D	0·142	0·113	2·1	24·3
E	0·221	0·0157	1·1	19·3
F	0·286	0·00403	0·9	19·2

(Curve *D* has been lowered by 1·0.)

Above this range of iodine concentration the activation energies increase with increasing iodine concentration, rising to 14·5 kcal. mole^{-1} for the forward runs at $7{\cdot}3 \times 10^{-2}$ mole l.$^{-1}$ of iodine, and 24·3 kcal. mole^{-1} for the reverse runs at a similar iodine concentration. It was not possible to use higher concentrations of iodine because these solutions were almost saturated.

(g) *Entropies of activation.* The entropies of activation $\Delta S_f^{\ddagger}$ and $\Delta S_r^{\ddagger}$ for the forward and the reverse reaction respectively have been found (as in Part II) for the range of unit iodine order and constant activation energy. The values thus obtained are given in Table 1.

TABLE 1. *The rate constants, activation energies, and entropies of activation, for the iodine-catalysed dimerisation of* 1 : 1-*diphenylethylene.**

Temp.	Rate constant	Activation energy (kcal. mole^{-1})	Entropy of activation (cal. mole^{-1} deg.$^{-1}$)
Forward reaction	k_f (mole^{-2} l.^{2} sec.$^{-1}$)	E_f	$-\Delta S_f^{\ddagger}$
33·8°	$2{\cdot}3 \times 10^{-4}$	$12{\cdot}3 \pm 0{\cdot}7$	38·1
45·9	$3{\cdot}2 \times 10^{-4}$		38·4
54·6	$4{\cdot}6 \times 10^{-4}$		39·0
Reverse reaction	k_r (mole^{-1} l. sec.$^{-1}$)	E_r	$-\Delta S_r^{\ddagger}$
33·8°	$2{\cdot}4 \times 10^{-6}$	$19{\cdot}4 \pm 0{\cdot}8$	23·8
45·9	$6{\cdot}9 \times 10^{-6}$		24·0
54·6	$1{\cdot}24 \times 10^{-5}$		24·3

* These figures only apply to solutions having an iodine concentration between 2×10^{-3} and 2×10^{-2} mole l.$^{-1}$, where the iodine order is unity (see text). The rates and entropies refer to the 1 mole l.$^{-1}$ standard state.

(h) *Volume changes during reaction.* Since the iodine orders for the forward and the reverse reaction are the same, the volume changes occurring from the initial to the equilibrium position of the system V_e, should be a function of the olefin concentration only, as in the dimerisations catalysed by trichloroacetic acid (Parts I and II). This is however found not to be the case; for the same weight of initial olefin the volume change in these reactions, V^*, is less at low iodine concentration than at high iodine concentration. Plots of V^*, for a given weight of initial olefin, against iodine concentration are curves of the type shown in Fig. 4.

If this dependence on the initial iodine concentration were due to differing iodine orders for the forward and reverse reactions, then the values of V^* starting from equal weights of monomer and dimer should be complementary, and their sum at any iodine concentration should be constant. This is not the case, however. For systems of low iodine concentration the same final monomer–dimer mixture is not obtained from two solutions of equal iodine concentration, one containing a given initial weight of monomer and the other the same initial weight of dimer.

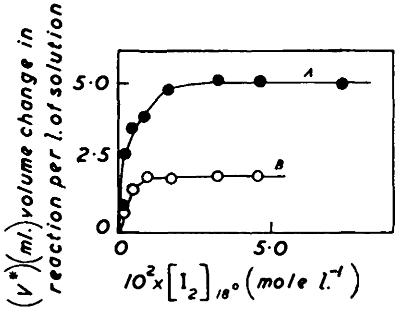
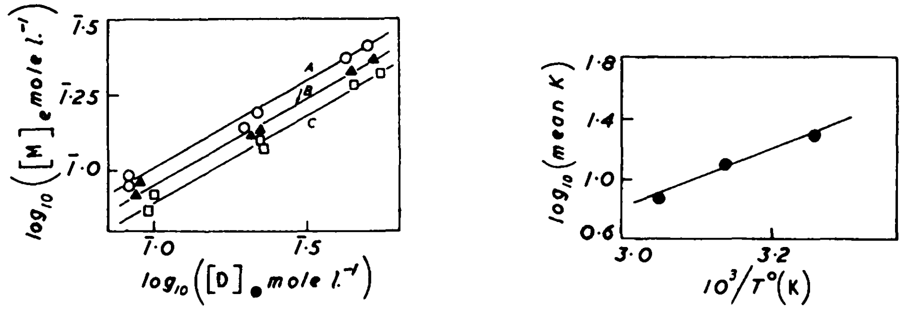


FIG. 4. *Dependence of V^* on iodine concn.*
A, Constant initial 1 : 1-*diphenylethylene concn.* 0·540 *mole* $l.^{-1}$ *at* 54·6°.
B, Constant initial 1 : 1 : 3 : 3-*tetraphenylbut*-1-*ene concn.* 0·285 *mole* $l.^{-1}$ *at* 54·6°.

FIG. 5. *Equilibrium concentrations of monomer and dimer, and the temperature-dependence of the equilibrium constant.*



(*a*) *Plot of* $\log_{10} [M]_e$ *against* $\log_{10} [D]_e$.
A, 54·6°, *slope* 0·5 ± 0·1.
B, 45·9°, *slope* 0·5 ± 0·1.
D, 33·8°, *slope* 0·5 ± 0·1.

(*b*) *Plot of* $\log_{10}$ (*mean K*) *against* $1/T$ (°K).

The monomer–dimer mixture which is obtained indicates that the reaction has stopped before complete equilibrium has been reached.

Since the sole product isolated from the reaction mixtures is the dimer, 1 : 1 : 3 : 3-tetraphenylbut-1-ene, and its concentration always agrees to within 5% with the observed volume change, the only possible explanation is that the iodine catalyst is converted in some way into an unreactive species, the reaction thus stopping short of equilibrium.

When the iodine concentration is sufficiently high, V^* becomes independent of it, as seen in Fig. 4 (where the iodine concentration is $>5\%$ of initial olefin). The sum of the forward and the reverse volume changes for equal initial weights of monomer and dimer is then constant at all three temperatures. If a true equilibrium is reached at these high iodine concentrations, these sums should be equal to the volume change accompanying complete conversion of monomer into dimer. The volume changes accompanying the complete conversion of 1·0 mole of monomer into 0·5 mole of but-1-ene in 1 l. of solution would, from these sums, be 12·5 ml. at 33·8°, 12·3 ml. at 45·9°, and 12·7 ml. at 54·6°. These values agree to within 2% with those found above from density measurements, thus confirming that a true equilibrium is attained at high iodine concentrations, (*i.e.*, $V^* = V_e$), and that the position of equilibrium is not then dependent on the iodine concentration.

(i) *Equilibrium constants.* The volume changes at high iodine concentration (when $V^* = V_e$) give a value for the concentration of dimer or monomer formed in the reaction when it reaches a true equilibrium. The concentrations of unchanged monomer or dimer can be calculated from their initial concentrations at the bath temperatures.

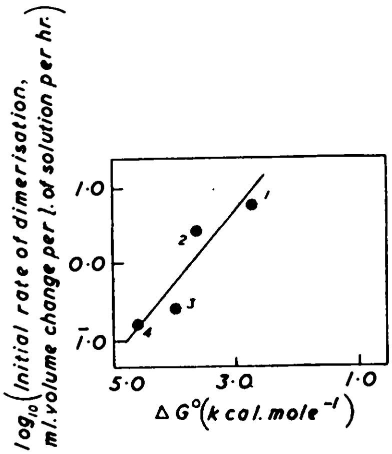


FIG. 6. *Variation of initial rate with solvent.*

Plot of $\log_{10}$ *(initial rate) at 54·6° for initial iodine concn. 0·076 mole l.*$^{-1}$ *and initial* 1 : 1-*diphenylethylene concn. 0·540 mole l.*$^{-1}$, *against the free-energy change,* $\Delta G°$, *for the ionisation of tri-*p*-tolylmethyl chloride.*

The numbers on the points signify the solvents : 1, PhNO_2; 2, Pr^iNO_2; 3, $m\text{-C}_6\text{H}_4\text{Me}\cdot\text{NO}_2$; 4, $(\text{CH}_2\text{Cl})_2$.

Thus for any solution the equilibrium concentrations of monomer $[\text{M}]_e$ and dimer $[\text{D}]_e$ can be obtained. A plot of $\log_{10} [\text{M}]_e$ against $\log_{10} [\text{D}]_e$ is given for each bath temperature in Fig. 5*a*. These plots are all straight lines of slope 0·5 ± 0·1. Thus as in Part II the equilibrium constant, K, for the dimerisation is given by :

$$K = [\text{D}]_e/[\text{M}]_e^2$$

The mean values of the equilibrium constants found in this way for solutions reaching true equilibrium are given in Table 2.

TABLE 2. *Thermodynamic constants for the dimerisation of* 1 : 1-*diphenylethylene.*

Catalyst	Solvent	K (°c) (mole^{-1} l.)	$-\Delta G°$ (kcal. mole^{-1})	$-\Delta H°$ (kcal. mole^{-1})	$-\Delta S°$ (cal. mole^{-1} deg.$^{-1}$)
I_2	Pr^iNO_2	18·5 (33·8°) 13·4 (45·9°) 7·0 (54·6°)	1·79 ± 0·05	9·7 ± 1·0	25·7 ± 5
$\text{CCl}_3\cdot\text{CO}_2\text{H}$ *	C_6H_6	15·9 (33·8°)	1·59 ± 0·05	10·0 ± 0·5	27·1 ± 2
$\text{CCl}_3\cdot\text{CO}_2\text{H}$ *	EtNO_2	13·4 (34·2°)	1·59 ± 0·05	9·7 ± 0·5	25·7 ± 2

* Taken from Parts I and II of this series.[1]

(j) *Exothermicity of the dimerisation.* A plot of $\log_{10}$ (mean K) against $1/T$°K was made, as shown in Fig. 5*b*, and the exothermicity ($-\Delta H°$) found from its slope to be 9·7 ± 1·0 kcal. mole^{-1} (see Table 2).

Effect of Solvent on the Dimerisation Rate.—A series of dilatometric runs was carried out at 54·6° with the solvents nitrobenzene, 2-nitropropane, *m*-nitrotoluene, and ethylene dichloride. The initial iodine (0·076 mole l.$^{-1}$) and initial 1 : 1-diphenylethylene (0·540 mole l.$^{-1}$) concentrations were identical in each solvent.

The initial rates were measured as previously outlined. Each of the solvents gave normal volume–time curves (volume decreasing with time) of the type shown in Fig. 1.

The contents of the dilatometers were analysed when the volume change ceased, and the product isolated in each case was shown by its m. p. (112—113°) to be 1 : 1 : 3 : 3-tetraphenylbut-1-ene.

A plot of $\log_{10}$ (initial rate of volume decrease per l. of solution) against the free energy change $\Delta G°$ for the ionisation of tri-*p*-tolylmethyl chloride in the same solvents[8] according to

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[8] Evans, Price, and Thomas, *Trans. Faraday Soc.*, (*a*) 1955, **51**, 481; (*b*) 1954, **50**, 470, 568; (*c*) 1956, **52**, 332.

the equation, $RCl \longrightarrow R^+Cl^-$ (Fig. 6), shows a roughly linear correlation. It must be stressed that this correlation is purely qualitative, since (i) the reagent orders may differ from solvent to solvent, and (ii) the volume changes accompanying dimerisation may differ slightly from solvent to solvent. The latter effect will not be large, as is shown by the close similarity of the volume changes accompanying complete dimerisation of 1 : 1-diphenylethylene in benzene,[1a] nitroethane,[1b] and nitropropane (this paper). The initial rates measured in rate of volume change per l. of solution will therefore give a reasonable measure of the initial rate of formation of dimer.

DISCUSSION

The Reaction Mechanism.—Any mechanism must account for the following observations. (*a*) The sole product of the iodine-catalysed dimerisation of 1 : 1-diphenylethylene is 1 : 1 : 3 : 3-tetraphenylbut-1-ene. (*b*) The dimerisation is reversible, not affected by light or by the surface of the reaction vessel. (*c*) The iodine titratable with sodium thiosulphate at the end of the reaction is equal, within experimental error ($\pm 3\%$), to the total initial iodine concentration. (*d*) The initial rate of the forward reaction is second ordei in total monomer. (*e*) The initial rate of the reverse reaction is first order in total dimer. (*f*) The initial rate of both the forward and the reverse reaction are of the same order with respect to total iodine; the value of this order is $1 \pm 0{\cdot}1$ for iodine concentrations between about 2×10^{-3} and 2×10^{-2} mole l.$^{-1}$, and rises rapidly to a value of 2·0 at iodine concentrations of about 10^{-1} mole l.$^{-1}$ (It is not experimentally possible to extend the iodine concentration further than the 200-fold range we have used.) (*g*) Over the experimental range studied, the monomer–dimer equilibrium is fully established for iodine concentrations greater than about 10^{-2} mole l.$^{-1}$. At iodine concentrations below this value, however, the monomer–dimer equilibrium is not established completely. This lack of equilibrium becomes more marked the lower the iodine concentration, although the total iodine can still be completely estimated by sodium thiosulphate.

These facts can be interpreted by the following reaction system :

$$C_s + M \underset{b}{\overset{a}{\rightleftharpoons}} (CM)_s^* \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$(CM)_s^* + M \underset{b}{\overset{a}{\rightleftharpoons}} (CD)_s^* \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$(CD)_s^* \underset{b}{\overset{a}{\rightleftharpoons}} C_s + D \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where M is monomer, D is dimer, C_s is the solvated catalyst, $(CM)_s^*$ and $(CD)_s^*$ are solvated polar intermediates formed by reaction of catalyst with monomer and of catalyst with dimer respectively. These equations will explain the experimental points (*a*), (*b*), (*d*), and (*e*), if we take reaction (2*a*) as rate-determining for the forward reaction, and reaction (2*b*) or (3*b*) as rate-determining for the reverse process. On this basis the following rate equations can be written :

$$\begin{aligned} \text{Rate of forward reaction} &= k_{2a}K_1[M]^2[C_s] \\ \text{Rate of reverse reaction} &= k_{2b}K_3^{-1}[D][C_s] \\ \text{or} &= k_{3b}[D][C_s] \end{aligned}$$

The order of the reaction in total iodine can be interpreted according to reactions (4) and (5), if I_2 and/or I^+I^- and $I^+I_3^-$ can act as the catalyst C.

$$I_2 \rightleftharpoons I^+I^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

$$I_2 + I_2 \rightleftharpoons I^+I_3^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

At low iodine concentrations the equilibrium (4) will predominate, and if the catalyst C_s were I_2 and/or I^+I^-, its kinetic effect would be of first order in total iodine. At high iodine concentrations the species $I^+I_3^-$ will predominate, and if this is acting as catalyst, C_s, its kinetic effect will be of second order in total iodine. This interpretation would necessitate the iodine order's remaining unity for all iodine concentrations lower than those studied, and rising to a maximum of 2 for all iodine concentrations higher than those used. As regards point (*g*), the lack of monomer–dimer equilibrium at low iodine concentrations suggests that iodine is slowly converted into a non-catalytic form, in which, however, it can be completely titrated with sodium thiosulphate. Since solutions of iodine in 2-nitropropane have always the same catalytic activity independent of the length of time they have been made up, it seems clear that the reaction of iodine which leads to its loss of catalytic activity is a reaction between it and the monomer or dimer :

$$C_s + M \rightleftharpoons (CM)_s\dagger \quad . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

or

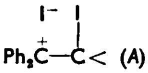
$$C_s + D \rightleftharpoons (CD)_s\dagger \quad . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

where the equilibria are well over to the right, and where $(CM)_s\dagger$ and $(CD)_s\dagger$ differ from the intermediates $(CM)_s^*$ and $(CD)_s^*$ of equation (1), (2), and (3) in the fact that they do not react further.

By analogy with the work of the previous Parts, where it was found for the acid-catalysed dimerisation that the active intermediate was the carbonium ion, we postulate that $(CM)_s^*$ and $(CD)_s^*$ are carbonium ions of the type (*A*) where the negative ion may be I^-, as written, or I_3^-, if $I^+I_3^-$ is acting as the catalyst (see reaction 5). Since the catalyst, however, is not a proton donor, this dimerisation differs from that of the acid-catalysed reaction (Parts I and II) in that the formation of the dimer involves migration of a hydrogen atom from one monomer to the other. If the carbonium ion postulated above is the active intermediate, there will also be an accompanying migration in the opposite direction of a covalently bonded iodine atom.

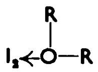
If $(CM)_s^*$ and $(CD)_s^*$ are carbonium ions, it seems plausible that the non-reactive species $(CM)_s\dagger$ and $(CD)_s\dagger$ should be π-complexes. In Part III we give evidence that the π-complex formed between acid and olefin is produced more slowly than is the carbonium ion, but its final equilibrium position lies much further over to the complex side. We therefore suggest that the iodine in solution is slowly converted into a π-complex with the olefin, the iodine acting as an electron-acceptor, and the olefinic double bond as an electron-donor. The possibility that the iodine is deactivated by forming an iodide with the olefin is unlikely (*a*) because the total iodine is titratable at the end of the experiment, and (*b*) because this iodide has never been isolated.

The more iodine in solution, the longer it would take for its concentration to be reduced sufficiently to stop the reaction, and the closer would the forward and the reverse reaction approach their true equilibrium positions. Eley and Richards [9] have studied the iodine-catalysed polymerisation of vinyl ethers and in order to interpret their results postulate three products of interaction between iodine and the vinyl ether :



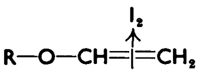
$\mathrm{Ph_2}\overset{I^-}{\overset{+}{C}}-\overset{I}{C}<$ (*A*)

(*a*)



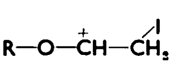
$I_2 \leftarrow \overset{R}{O}-R$

(*b*)



$R-O-CH=\overset{I_2}{\uparrow}=CH_2$

(*c*)



$R-O-\overset{+}{C}H-\overset{I}{C}H_2$

These authors conclude that the carbonium ion (*c*) is the reactive intermediate in the polymerisation, while the π-complex (*b*) is also present as an unreactive species which has the effect of reducing the concentration of active iodine. The catalytically active iodine is taken to be I^+ produced by the interaction of two molecules of type (*a*).

Rate and Equilibrium Constants.—It can be seen from Tables 1 and 2 that the ratio of the rate constants differs considerably from the overall equilibrium constant for the dimerisation. As will be described in a later paper, we find that there is extensive complex-formation between the iodine and the benzene rings of the monomer and the olefinic dimer,

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[9] Eley and Richards, *Trans. Faraday Soc.*, 1949, **45**, 425; Eley and Saunders, *J.*, 1952, 4167.

and we believe that the solvation of the catalyst, C(I_2, and/or I^+I^-, and $I^+I_3^-$) consists mainly of this type of complex-formation. The catalyst for the initial stage of the forward reaction will therefore be different from that for the initial stage of the reverse reaction, and thus the ratio of the initial rate constants k_f/k_r will not be equal to K. These reactive benzene–iodine complexes are similar in type to that postulated by Eley and Richards [see structure (*a*) above].

One of us (P. M. S. J.) thanks the Department of Scientific and Industrial Research for a maintenance allowance.

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[*Received, December 27th,* 1956.]