THE DIMERIZATION OF 1 : 1-DIPHENYLETHYLENE

PART 1.—HEAT OF DIMERIZATION

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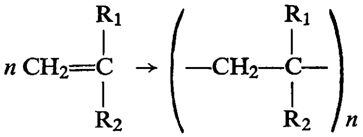
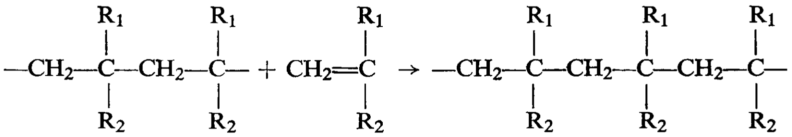
The value of ΔH for the conversion of two moles of 1 : 1-diphenylethylene (DPE) into 1 : 1 : 3 : 3-tetraphenylbut-1-ene (TPB) in CCl_4 solution using $SnCl_4$ as catalyst and HCl as co-catalyst has been measured (i) calorimetrically and (ii) from the values of the equilibrium constant determined at 25, 35 and 45° C. The values are in good agreement. The result, $\Delta H = -12{\cdot}1$ kcal/mole, suggests that the reaction is 7·1 kcal/mole less exothermic than it would be in the absence of steric interference between the substituents in TPB.

The value of ΔH for the reaction



$$n\,CH_2{=}\underset{R_2}{\overset{R_1}{C}} \rightarrow \left(-CH_2-\underset{R_2}{\overset{R_1}{C}}-\right)_n$$

is negative and its value has been previously shown [1, 2] to depend upon the sizes of the substituents R_1 and R_2. This dependence arises from the fact that the polymerization generally proceeds by a " head-to-tail " mechanism:



$$-CH_2-\underset{R_2}{\overset{R_1}{C}}-CH_2-\underset{R_2}{\overset{R_1}{C}}- + CH_2{=}\underset{R_2}{\overset{R_1}{C}} \rightarrow -CH_2-\underset{R_2}{\overset{R_1}{C}}-CH_2-\underset{R_2}{\overset{R_1}{C}}-CH_2-\underset{R_2}{\overset{R_1}{C}}-$$

The substituents on neighbouring C atoms in the chain interfere sterically with one another thereby weakening the C—C bonds in the chain and the polymerization is, as a result, less exothermic than it would be in the absence of steric hindrance. The extent of the reduction in the exothermicity of polymerization will depend upon the sizes of the substituents. It sometimes happens that the magnitude of the steric effect is so great that polymers greater in size than the dimer cannot be obtained. Such is the case when R_1 and R_2 are methyl and *neo*-pentyl groups respectively,[3] or when R_1 and R_2 are phenyl groups. In this case, however, resonance between the phenyl substituents and the ethylenic linkage exerts an influence on the value of ΔH as well as steric hindrance. An attempt will be made to assess the influence of both factors on the exothermicity of the reaction.

EXPERIMENTAL

PURIFICATION OF MATERIALS

1 : 1-Diphenylethylene (DPE), prepared according to ref. (4), was purified by distillation from alumina or silica gel to remove diphenylmethylcarbinol. It was then repeatedly fractionally distilled using a magnetically stirred distillation flask and a heated 3-ft. column packed with gauze rings. The reflux ratio was 15 : 1. CCl_4 of B.P. quality was purified by allowing it to stand in contact with $CaCl_2$ and NaOH, fractionating using a 5-ft. column packed with Fenske helices and collecting the fraction of b.p. 76·5-77° C. $SnCl_4$ was purified as required by distilling from Ca under reduced pressure. HCl was prepared by dropping concentrated sulphuric acid on to a mixture of NaCl and concentrated hydrochloric acid and dried by passing through concentrated sulphuric acid. The $K_2Cr_2O_7$, $KBrO_3$ and KIO_3 used were of A.R. quality. The $Na_2S_2O_3$, KBr, KI and $HgCl_2$ used were of B.P. quality.

CALORIMETRY

The apparatus was as shown in fig. 1. The calorimeter, which consisted of a lagged Dewar flask was immersed in a thermostat maintained at 25 ± 0·05° C. A large rubber stopper carried the fittings shown. A known weight of DPE was introduced into the calorimeter and the apparatus swept out with dry, oxygen-free nitrogen. The temperature-controlled burette (7) was filled with the CCl_4 solution of HCl using the N_2 supply and the solution allowed to remain therein until it acquired the temperature of the jacket. (The purpose of the jacket was to ensure that the thermostat temperature was roughly midway between the initial and final temperatures of the calorimeter contents.) The solution was then run into the calorimeter. $SnCl_4$ was freshly distilled under reduced pressure into burette (6) and the reaction started by running a known volume into the calorimeter. The temperature rise was measured using the Beckmann thermometer (8).

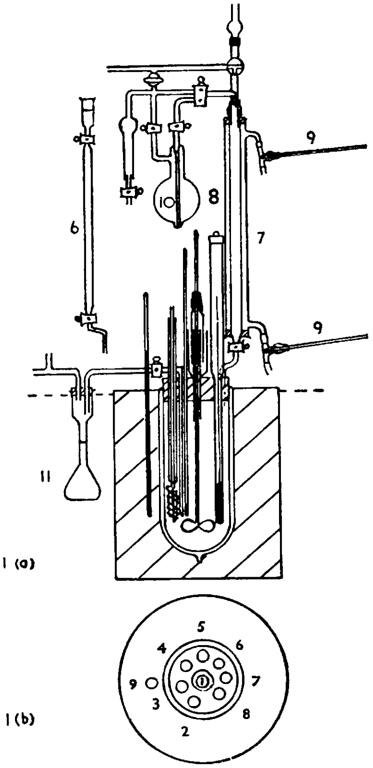


FIG. 1.

(*a*) Calorimeter.

1. mercury seal stirrer,
2. thermometer 10-30° in 0·1° C,
3. N_2 inlet, sample outlet,
4. heater,
5. N_2 outlet,
6. $SnCl_4$ burette,
7. CCl_4 burette,
8. Beckmann thermometer,
9. thermometers,
10. CCl_4+HCl reservoir,
11. sample flask.

(*b*) Plan of rubber stopper.

Since the reaction does not go to completion, samples were removed for analysis when the temperature reached its maximum value, by forcing liquid up through the outlet tube (3) into a weighed graduated flask (11). The heat capacity of the calorimeter and contents was determined electrically the following day when the reaction was completed, a correction being made for the weight of the sample removed. The cooling correction was made by the conventional method of measuring the area under the temperature against time curve.

EQUILIBRIUM MEASUREMENTS

The equilibrium 2 DPE $\rightleftharpoons$ TPB is established slowly. In the equilibrium experiments known amounts of either DPE or TPB and $SnCl_4$ were placed in graduated flasks which were then filled up to the graduation marks with CCl_4. Three sets of flasks were used which were maintained in thermostats at 25°, 35° and 45° C ± 0·05° C for 9, 6 and 5 months respectively. After these lengths of time equilibrium was established as shown by the fact that the same values of K_c were obtained starting with TPB initially as by starting with DPE. The flasks were removed from the thermostats and their contents analyzed as described below.

ANALYSIS

The analysis depends upon the authors' observation that Br_2 adds to the ethylenic linkage in DPE but not to that in TPB. It was shown that $SnCl_4$ catalyzes the substitution of Br_2 in both DPE and TPB (cf. Williams [5]) and must therefore be removed before analysis. After trials using ether [6] and dioxan, the method finally adopted involved shaking with water to decompose the $SnCl_4$, separating the CCl_4 layer from the aqueous emulsion and repeatedly extracting the latter with quantities of CCl_4 to avoid loss of DPE. Aliquots of the CCl_4 solution were analyzed by one of the following methods. The different methods gave consistent results and had an accuracy of better than 1 %.

(i) The aliquot was treated with 1½-2 times the amount of a CCl_4 solution of Br_2 needed for complete addition and left in the dark for 1-1½ h. KI solution was added and the I_2 liberated estimated with standard $Na_2S_2O_3$ solution. The extent of substitution was determined by adding KIO_3 and estimating the additional quantity of I_2 liberated.

(ii) Conductimetrically using the method [7] of Dubois and Skoog.

(iii) The aliquot was treated with a glacial acetic acid solution of Br_2 in similar excess to that of (i). The addition in this case takes place rapidly and the estimation of the excess Br_2 was made immediately.

RESULTS

CALORIMETRY

The results are shown in table 1, from which the mean value of ΔH for the conversion of two moles of DPE into TPB is given by

$$\Delta H = -12{\cdot}1 \pm 0{\cdot}4 \text{ kcal.}$$

TABLE 1

expt.	no. of moles $SnCl_4 \times 10^2$	no. of moles DPE initially $\times 10^2$	no. of moles DPE finally $\times 10^2$	heat loss correction °C	corrected temp. rise in °C	heat capacity of calorimeter and contents in cal/deg.	ΔH for dimerization of 2 moles DPE in kcal
1	8·37	8·46	3·21	0·05	3·29	95·8	− 12·0
2	18·89	9·40	2·97	0·22	3·96	103·0	− 12·7
3	12·36	8·77	3·16	0·07	3·38	95·9	− 11·6
4	16·66	9·02	2·70	0·10	3·72	103·3	− 12·1
5	19·08	8·63	2·89	0·24	3·39	105·0	− 12·4
6	19·77	9·24	2·97	0·10	3·34	109·6	− 11·7

EQUILIBRIUM MEASUREMENTS

The results of the equilibrium experiments are shown in table 2. The mean values of K_c at 25, 35 and 45° C respectively can be shown to satisfy best the equation

$$\log_{10} K_c = (2624{\cdot}5/T) - 7{\cdot}2431. \qquad (1)$$

From eqn. (1), the value of ΔH can be calculated to be

$$\Delta H = -\ 12 \pm 2\ \text{kcal.}$$

Thus the value of ΔH obtained from equilibrium measurements is in good agreement with the more precise value obtained calorimetrically

TABLE 2

expt.	no. of moles TPB × 10^4	no. of moles DPE × 10^4	vol. of solution (ml)	K_c
MEASUREMENTS AT 25° C				
1	7·46	7·04	25	38
2	5·37	6·04	25	37
3	5·14	6·11	25	34
4	6·24	6·40	25	38
5	6·76	6·40	25	41

mean value of $K_c = 38 \pm 2$;
value of K_c from eqn. (1) = 36.

expt.	no. of moles TPB × 10^4	no. of moles DPE × 10^4	vol. of solution (ml)	K_c
MEASUREMENTS AT 35° C				
1	16·9	13·7	20	18·1
2	26·6	17·9	20	16·7
3	27·7	18·1	20	17·0
4	32·2	19·1	20	17·6
5	10·9	11·5	20	16·6
6	16·4	14·0	20	16·6
7	24·6	16·9	20	17·2

mean value of $K_c = 17{\cdot}1 \pm 0{\cdot}5$;
value of K_c calc. from eqn. (1) = 18·6.

expt.	no. of moles TPB × 10^4	no. of moles DPE × 10^4	vol. of solution (ml)	K_c
MEASUREMENTS AT 45° C				
1	15·6	19·1	25·7	11·1
2	5·08	8·84	18·6	12·0
3	14·3	18·0	23·6	10·4
4	9·40	16·2	24·7	8·8

mean value of $K_c = 10{\cdot}5 \pm 1$;
value of K_c calc. from eqn. (1) = 10.

VALUE OF ΔH FOR THE REACTION $2\,Ph_2C = CH_2(g) \rightarrow Ph_2C = CH\,.\,CPh_2\,.\,CH_3(g)$ is then obtained as follows. It can be assumed that the value of ΔH for the reaction

$$2\,Ph_2C{=}CH_2(l) \rightarrow Ph_2C{=}CH\,.\,C(Ph)_2CH_3(l)$$

will not differ greatly from the value for the reaction taking place in CCl_4 solution. Vapour pressure measurements [14] yield the following data:

$Ph_2C{=}CH_2(l) \rightarrow Ph_2C{=}CH_2(g)$ $\qquad \Delta H = 17{\cdot}52$ kcal/mole,

$Ph_2C{=}CH\,.\,CPh_2\,.\,CH_3(l) \rightarrow Ph_2C{=}CH\,.\,CPh_2\,.\,CH_3(g)$ $\qquad \Delta H = 22{\cdot}25$ kcal/mole.

Hence for the reaction:

$$2\,Ph_2C{=}CH_2(g) \rightarrow Ph_2C{=}CH\,.\,CPh_2\,.\,CH_3(g)$$

the value of ΔH is given by

$$\Delta H = -\ 24{\cdot}9\ \text{kcal.}$$

DISCUSSION

The value of ΔH for the reaction

$$2Ph_2C{=}CH_2(g) \rightarrow Ph_2C{=}CH\,.\,CPh_2\,.\,CH_3(g)$$

will differ from that for the reaction

$$2CH_2{=}CH_2(g) \rightarrow CH_2{=}CH\,.\,CH_2\,.\,CH_3(g)$$

for two reasons :—

(i) Resonance between the C_6H_5 groups and the ethylenic linkage which will lead to a weakening of the π-bond and will therefore result in making the dimerization of DPE more exothermic than it would be in the absence of such resonance. The resonance between the two C_6H_5 groups on C_1 of TPB and the ethylenic linkage will be roughly as strong as that in DPE since, as can be seen from the Fischer-Stuart models (fig. 2), the extent to which these groups are displaced from coplanarity with $> C = C$ is about the same in both molecules. It can therefore be assumed that the resonance energy will be the same in both cases.

(ii) Steric interference between the C_6H_5 groups on C_1 and those on C_3 of TPB will lead to a weakening of those C—C bonds between C_1 and C_3 in the molecule, and hence tend to make the reaction less exothermic than it would be in the absence of steric hindrance.

The calculation of the magnitudes of effects (i) and (ii) is subdivided as follows:

(*a*) *The contribution to the total resonance energy in* DPE *due to resonance between the benzene rings and the ethylenic linkage.* Wheland[8] has calculated values for the resonance energies of benzene (R_b), styrene (R_s) and DPE (R_d) from which it may be shown that

$$\frac{R_d - 2R_b}{R_s - R_b} = 1{\cdot}7.$$

This value for the ratio may be used to calculate the value of $R_d - 2R_b$, which is the contribution (i), from the value of $R_s - R_b$ which is derived from the following thermochemical data obtained at 25° C:

$$CH_2{=}CH_2(g) + H_2 \rightarrow CH_3CH_3(g),$$
$$\Delta H = -\ 32{\cdot}732 \pm 0{\cdot}133 \text{ kcal/mole (ref. (9))}$$

$$Ph\,.\,CH{=}CH_2(l) + H_2 \rightarrow Ph\,.\,CH_2CH_3(l)$$
$$\Delta H = -\ 27{\cdot}87 \text{ kcal/mole}$$

obtained from the following combustion measurements:

$$Ph\,.\,CH_2CH_3(l) + 10\tfrac{1}{2}O_2(g) \rightarrow 8CO_2(g) + 5H_2O(l)$$
$$\Delta H = -\ 1091{\cdot}03 \pm 0{\cdot}17 \text{ kcal/mole (ref. (10))}$$

$$Ph\,.\,CH{=}CH_2(l) + 10O_2(g) \rightarrow 8CO_2(g) + 4H_2O(l)$$
$$\Delta H = -\ 1050{\cdot}58 \pm 0{\cdot}14 \text{ kcal/mole (ref. (11))}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l)$$
$$\Delta H = -\ 68{\cdot}3174 \pm 0{\cdot}0096 \text{ kcal/mole (ref. 12))}$$

$$CH_3\,.\,CH_2\,.\,Ph(l) \rightarrow CH_3\,.\,CH_2\,.\,Ph(g)$$
$$\Delta H = 10{\cdot}10 \text{ kcal/mole (ref. (10))}$$

$$CH_2{=}CH\,.\,Ph(l) \rightarrow CH_2 = CH\,.\,Ph(g)$$
$$\Delta H = 10{\cdot}69 \text{ kcal/mole (ref. (13)}$$

hence

$$PhCH{=}CH_2(g) + H_2(g) \rightarrow Ph\,.\,CH_2\,.\,CH_3(g)$$
$$\Delta H - -\ 28{\cdot}46 \text{ kcal/mole.}$$

FIG. 2.—(*a*) Model of TPB; (*b*) model of DPE.

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Hence

$$R_s - R_b = 32{\cdot}73 - 28{\cdot}46, \; = 4{\cdot}27 \text{ kcal/mole}$$

and

$$R_d - 2R_b = 1{\cdot}7 \times 4{\cdot}27 = 7{\cdot}26 \text{ kcal/mole.}$$

(*b*) The value of ΔH for the reaction,

$$2\text{Ph}_2\text{C}{=}\text{CH}_2(g) \rightarrow \text{Ph}_2\text{C}{=}\text{CH}\,.\,\text{CPh}_2\,.\,\text{CH}_3(g),$$

if the TPB molecule were sterically unhindered may be calculated from the following data:

$$2\text{CH}_2{=}\text{CH}_2(g) \rightarrow \text{CH}_2{=}\text{CH}\,.\,\text{CH}_2\,.\,\text{CH}_3(g)$$

$$\Delta H = -\,24{\cdot}7 \text{ kcal}$$

obtained from the following combustion measurements:

$$\text{CH}_2{=}\text{CH}\,.\,\text{CH}_2\,.\,\text{CH}_3(g) + 6\text{O}_2(g) \rightarrow 4\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$$

$$\Delta H = -\,649{\cdot}8 \pm 0{\cdot}2 \text{ kcal/mole (ref. (9))}$$

$$\text{CH}_2{=}\text{CH}_2(g) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 2\text{H}_2\text{O}(l)$$

$$\Delta H = -\,337{\cdot}23 \pm 0{\cdot}07 \text{ kcal/mole (ref. (9)).}$$

and

$$R_d - 2R_b = 7{\cdot}26 \text{ kcal/mole.}$$

Hence, for the sterically unhindered reaction,

$$2\text{Ph}_2\text{C} = \text{CH}_2(g) \rightarrow \text{Ph}_2\text{C} = \text{CH}\,.\,\text{CPh}_2\,.\,\text{CH}_3(g),$$

the value of ΔH is given by

$$\Delta H = -\,24{\cdot}7 - 7{\cdot}3 = -\,32{\cdot}0 \text{ kcal.}$$

When this calculated value is compared with the experimental value, it is seen that the existence of steric hindrance within the dimer has reduced the exothermicity of reaction by 32·0 − 24·9 = 7·1 kcal/mole. Thus the presence of steric interference between the substituents in TPB exerts a considerable effect on the exothermicity of the dimerization of DPE.

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