The Activation of Carbon–Carbon Double Bonds by Cationic Catalysts. Part I. The Dimerization of 1 : 1-Diphenylethylene.

By ALWYN G. EVANS, N. JONES, and J. H. THOMAS.

[Reprint Order No. 6029.]

The dimerization of 1 : 1-diphenylethylene to 1 : 1 : 3 : 3-tetraphenylbut-1-ene and the reverse reaction have been followed dilatometrically, with trichloroacetic acid as catalyst and benzene as solvent. The forward and the reverse reaction proceed to an equilibrium in which monomer and dimer are present, the same equilibrium being reached from either direction. The rate-determining step for the dimerization is the reaction of a monomer ion with a monomer molecule. The rate-determining step for the reverse reaction is the breakdown of a dimer ion. The formation of the monomer ion and the dimer ion involves three trichloroacetic acid molecules, one of which donates the proton to the olefin, the other two contributing to the solvation of the ion pair so formed.

The activation energies of the forward and the reverse reaction have been determined, and the heat of reaction has been obtained from the variation of the equilibrium constant with temperature.

IT has been shown that unless a cocatalyst, *e.g.*, water, is present *iso*butene is not polymerized by boron trifluoride (A. G. Evans and Polanyi, *J.*, 1947, 252; A. G. Evans and Meadows, *Trans. Faraday Soc.*, 1950, **46**, 327) or by titanium tetrachloride (Plesch, Polanyi, and Skinner, *J.*, 1947, 257). In the presence of water the olefin is activated by accepting a proton from the chloride–water complex (for references see A. G. Evans, *J. Appl. Chem.*, 1951, **1**, 240). To investigate further this type of double-bond activation we have studied dilatometrically the reaction of 1 : 1-diphenylethylene in benzene when catalysed by trichloroacetic acid. Cationic catalysts bring about dimerization of this olefin (Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021), polymerization to products of higher molecular weight being sterically impossible because of the bulky phenyl groups. Thus this reaction is very suitable for investigations of the mechanism by which cationic catalysts activate carbon–carbon double bonds.

EXPERIMENTAL

Materials.—Trichloroacetic acid (from B.D.H.) was purified by two distillations in a high vacuum, collected under a high vacuum and stored in sealed ampoules.

1 : 1-Diphenylethylene (from Messrs. Mersey Chemicals Ltd.) was distilled under reduced pressure through a 25-cm. point column, then distilled from potassium hydroxide pellets in a one-piece all-glass apparatus under a high vacuum.

1 : 1 : 3 : 3-Tetraphenylbut-1-ene was obtained by dissolving 1 : 1-diphenylethylene in glacial

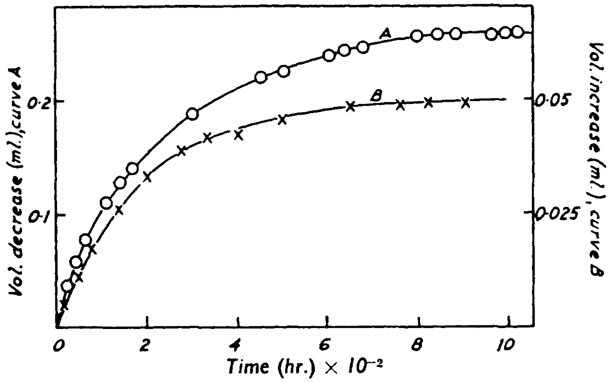
[redacted]

totally immersed in the thermostat, and the volume of the solution observed at appropriate times. The concentrations of the reactants were chosen so that no appreciable volume change could occur in the time required to make up the solution, fill the dilatometer, and bring the system to the temperature of the thermostat. Some experiments in which the solution was completely freed from air on the high-vacuum line by repeated cooling and pumping out gave results identical with those carried out as described above.

RESULTS

Dimerization of 1 : 1-*Diphenylethylene*.—(i) *Analysis of products*. The volume of the diphenylethylene–trichloroacetic acid–benzene mixture decreased gradually to constancy. In the absence of acid no change was detected during several weeks. An example of the plots obtained for volume decrease against time is shown in Fig. 1, curve *A*. After the reaction the dilatometer was broken and the trichloroacetic acid extracted in water and estimated by titration with alkali: no change in the acid concentration ever occurred. The benzene was removed from the non-aqueous layer by pumping in a high vacuum, and the residue was washed with methanol to remove unchanged 1 : 1-diphenylethylene, leaving crystals, m. p. 113° unchanged on crystallization from light petroleum (b. p. 60—80°); the material was thus established as 1 : 1 : 3 : 3-tetraphenylbut-1-ene. This also established that the dimer, 1-methyl-1 : 3 : 3-triphenylindane (which is produced from 1 : 1-diphenylethylene under certain conditions; Schoepfle and Ryan, *loc. cit.*) was not formed in our experiments, since this is very much less soluble in benzene and has m. p. 143°.

FIG. 1. *Volume change during reaction at* 33·8°.



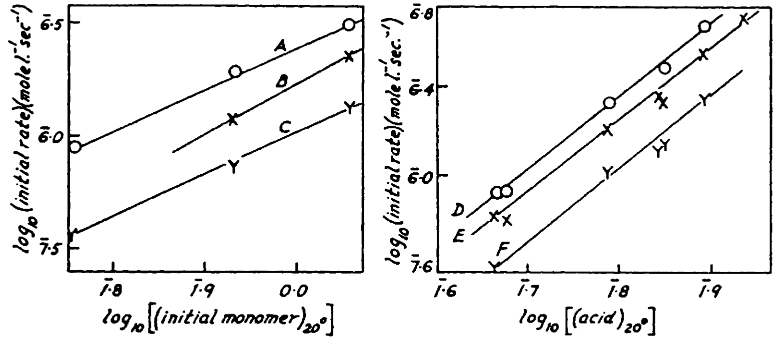
Reaction of:	*A*, monomer	*B*, dimer
Initial vol. (ml.) of solution	22·78	24·37
Initial concn. (mole $l.^{-1}$)	1·142 (monomer)	0·5555 (dimer)
Initial acid concn. (mole $l.^{-1}$)	0·709	0·768

The dimer formed was less than corresponded to complete reaction. This was further investigated as follows. Solutions of monomer in benzene, and of dimer in benzene, were made up, the same weight of olefin being added to the same volume of benzene in each case. The densities of these two solutions were measured at different temperatures. From the difference in the densities, the volume change was determined for the complete conversion from monomer to dimer for a given concentration and at a given temperature. A more accurate method of measuring this volume change in the presence of the acid was developed when the order of the reaction was known. This method, described below, gave the following values for the conversion of one mole of monomer into dimer: 11·85 ml. at 33·8°, 11·70 ml. at 45·7°, and 12·57 ml. at 54·7°. These agree within 4% with those obtained from the density measurements. The percentage reaction calculated, by assuming a linear relation for the change of volume with conversion of monomer into dimer, was the same as that obtained from the analysis of the products at equilibrium. For example, for the reaction shown in Fig. 1, curve *A*, the amount of dimer present at the end of the reaction was found to be 0·483 mole/l. by the volume change method and 0·465 mole/l. by the analysis of the products. Thus the reaction proceeds to an equilibrium position, in which the only dimer present is 1 : 1 : 3 : 3-tetraphenylbut-1-ene. This point was completely established, as described below, by experiments on the reverse reaction.

(ii) *Analysis of reaction curves.* Because the reaction does not go to completion, we analysed the rate curves by obtaining the initial rate of the reaction from the initial slope. This method is quite accurate in these experiments since the reactions are slow.

(iii) *Orders in monomer and in acid.* The dependence of the initial rate on initial monomer concentration (at constant acid concentration), and on acid concentration (at constant initial monomer concentration), are given in Figs. 2*a* and *b* respectively for different temperatures.

FIGS. 2*a and b*. *Orders in monomer and acid.*



Curve	Temp.			Slope
A	54·7°	Acid concn. (mole l.$^{-1}$)	0·677	1·85
B	45·7	Acid concn. (mole l.$^{-1}$)	0·685	2·2
C	33·8	Acid concn. (mole l.$^{-1}$)	0·692	1·9
D	54·7	Monomer concn. (mole l.$^{-1}$)	1·092	3·12
E	45·7	Monomer concn. (mole l.$^{-1}$)	1·108	3·10
F	33·8	Monomer concn. (mole l.$^{-1}$)	1·121	3·15

Concentrations have been evaluated from the coefficient of expansion of benzene (Int. Crit. Tables, Vol. VI, p. 85), also used for Fig. 4.

We find by this method that the order of reaction is 2·0 ± 0·2 in monomer and 3·1 ± 0·1 in acid.

(iv) *Temperature-dependence.* Fig. 2 contains all the data required to yield the temperature dependence of the initial rate at constant acid and constant initial monomer concentration. A typical result is given in Fig. 3. The average value of the activation energy for the forward reaction obtained from plots of this type is 9·1 ± 0·5 kcal./mole.

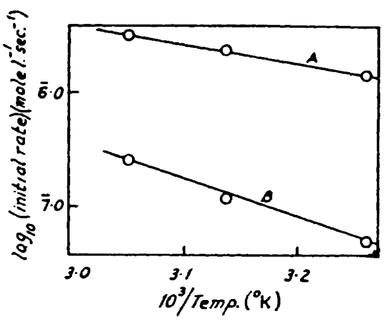


FIG. 3. *Temperature-dependence of initial rates.*
A, Dimerization reaction.
B, Reverse reaction.

Formation of Monomer from 1 : 1 : 3 : 3-*Tetraphenylbut*-1-*ene in Benzene*.—(i) *Analysis of products.* The volume of tetraphenylbut-1-ene–trichloroacetic acid–benzene systems increased gradually to constancy, as exemplified in Fig. 1, curve *B*. In the absence of acid no change in volume could be detected during several weeks. After reaction, the system was analysed in the same way as for the forward reaction : again no change in acid content was observed, and the amount of 1 : 1 : 3 : 3-tetraphenylbut-1-ene recovered (m. p. 113°) corresponded with that calculated from the observed volume change. For example, at 33·8° the amount of 1 : 1 : 3 : 3-tetraphenylbut-1-ene at equilibrium was 0·357 mole/l. by analysis, and 0·342 mole/l. by estimation from the volume change. This again establishes that none of the dimer, 1-methyl-1 : 3 : 3-triphenylindane, is formed in our experiments.

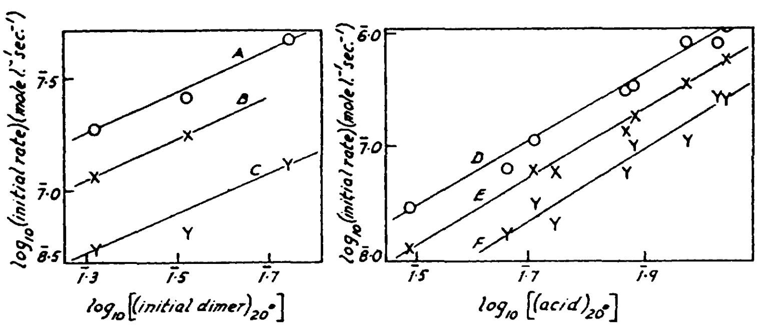
(ii) *Order in dimer and in acid.* The curves were analysed as for the forward runs, and the dependence of initial rate on initial monomer concentration (at constant acid concentration), and on acid concentration (at constant initial monomer concentration), is shown in Fig. 4 for different temperatures. It is seen that the order of reaction is 0·9 ± 0·2 in 1 : 1 : 3 : 3-tetraphenylbut-1-ene, and 3·0 ± 0·2 in acid. The scatter on these plots is more marked than for the forward reactions. These orders are again seen to be independent of temperature.

(iii) *Temperature-dependence.* In Fig. 3, curve *B*, is shown a typical result for the temperature-dependence of initial slope, obtained from the data of Fig. 4 as described for the forward run. The average value of the activation energy for this reverse reaction, E_r, obtained from plots of this type is 17·3 ± 1·5 kcal./mole.

Determination of Equilibrium Constant.—Since the forward and the reverse reaction are of the same order in acid, the value of the equilibrium constant, *K*, can be obtained from the equilibrium concentrations of monomer and dimer by using the expression $K = [\text{dimer}]_e/[\text{monomer}]_e^2$.

Thence the volume change, *x*, associated with the complete conversion of 1 mole of monomer into dimer has been found as follows. The value for *K* can be expressed in terms of *x* and the observed volume change of either the forward or the reverse reaction. By equating these alternative expressions values of *x* were obtained which were the same within ±1·5% for several pairs of forward and backward reactions. This establishes that true equilibrium is reached from both directions. Knowing the volume change for the complete conversion of monomer into dimer we have determined the equilibrium concentrations of these two olefins and thence the equilibrium constant, *K*, according to the above equation (see Table 1). *K* was reproducible within ±2·5% at each temperature. Further, the knowledge of the volume change for complete conversion of monomer into dimer together with the information obtained about the order in olefin and acid of the forward and reverse reactions enables us to convert the values of the initial slopes of the reaction curves into rate constants. These values are given in Table 1 where k_f is the rate constant for the forward reaction and k_r that for the reverse reaction, calculated from the expressions :

FIGS. 4*a and b*. *Orders in dimer and acid.*



Curve	Temp.			Slope
A	54·7°	Acid concn. (mole l.⁻¹)	0·735	0·92
B	45·7	Acid concn. (mole l.⁻¹)	0·745	0·90
C	33·8	Acid concn. (mole l.⁻¹)	0·754	0·90
D	54·7	Dimer concn. (mole l.⁻¹)	0·3987	2·90
E	45·7	Dimer concn. (mole l.⁻¹)	0·4039	2·98
F	33·8	Dimer concn. (mole l.⁻¹)	0·4091	3·08

$$\text{Initial rate of forward reaction} = k_f\,[\text{acid}]^{3\cdot1} \times [\text{initial monomer}]^2$$

$$\text{Initial rate of reverse reaction} = k_r\,[\text{acid}]^{3\cdot1} \times [\text{initial dimer}]$$

Since trichloroacetic acid exists completely in the dimer form in benzene (Bell and Arnold, *J.*, 1935, 1432), we have used the molecular weight of the acid dimer in evaluating the velocity constants.

Plotting the change of $\log_{10} K$ with $1/T$ (Fig. 5) gives a good straight line and the value of the exothermicity of reaction, *Q*, obtained from the slope of the line is 10·1 ± 0·5 kcal./mole.

Action of Trichloroacetic Acid as a Solvent.—The high order in trichloroacetic acid found in these experiments suggests that it is behaving in a dual capacity, as proton donor, and as solvent for the ions so produced. To examine the ability of this acid to cause ionization, in circumstances where no proton addition to a double bond can occur, it was added to benzene solutions of triphenylmethyl chloride and tri-*p*-tolylmethyl chloride. These solutions were so dilute that in the absence of trichloroacetic acid they were colourless. On addition of a very small amount of the acid, the yellow colour characteristic of the triarylmethyl ion was produced. This was established by measuring the spectrum of the solution (cf. *e.g.*, Fig. 6).

FIG. 5. *Temperature-dependence of equilibrium constant.*

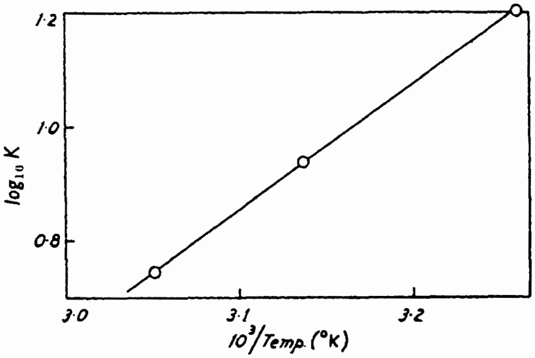
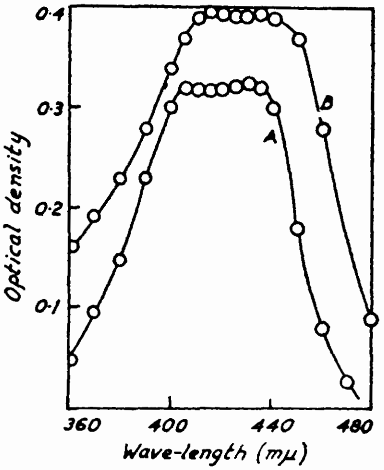


FIG. 6. *Spectrum of triphenylmethylcarbonium ion.*



A, $CPh_3{\cdot}OH$ in 98% H_2SO_4 ($8{\cdot}9 \times 10^{-6}$ mole l.$^{-1}$).
B, CPh_3Cl ($5{\cdot}59 \times 10^{-3}$ mole l.$^{-1}$), and $CCl_3{\cdot}CO_2H$ ($1{\cdot}32 \times 10^{-1}$ mole l.$^{-1}$) in benzene at 18°.

DISCUSSION

Reaction Mechanism.—The mechanism must be in accord with the following experimental results. (*a*) The dimerization reaction of 1 : 1-diphenylethylene to 1 : 1 : 3 : 3-tetraphenylbut-1-ene is of second order in monomer, and of third order in trichloroacetic acid. (*b*) The formation of 1 : 1-diphenylethylene from 1 : 1 : 3 : 3-tetraphenylbut-1-ene is of first order in dimer and of third order in trichloroacetic acid. We interpret these results according to the annexed scheme.

$$3AH + CH_2{:}CPh_2 \underset{b}{\overset{a}{\rightleftharpoons}} (Me{\cdot}CPh_2{}^+A^-)_{\text{solv. 2AH}}$$

$$(Me{\cdot}CPh_2{}^+A^-)_{\text{solv. 2AH}} + CH_2{:}CPh_2 \underset{b}{\overset{a}{\rightleftharpoons}} (Me{\cdot}CPh_2{\cdot}CH_2{\cdot}CPh_2{}^+A^-)_{\text{solv. 2AH}}$$

$$(Me{\cdot}CPh_2{\cdot}CH_2{\cdot}CPh_2{}^+A^-)_{\text{solv. 2AH}} \underset{b}{\overset{a}{\rightleftharpoons}} Me{\cdot}CPh_2{\cdot}CH{:}CPh_2 + 3AH$$

where AH is trichloroacetic acid, and the solvation of the ion pairs includes 2AH molecules.

We may write this more simply as:

$$3AH + M \underset{b}{\overset{a}{\rightleftharpoons}} (HM^+A^-)_{\text{solv. 2AH}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$(HM^+A^-)_{\text{solv. 2AH}} + M \underset{b}{\overset{a}{\rightleftharpoons}} (HD^+A^-)_{\text{solv. 2AH}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$(HD^+A^-)_{\text{solv. 2AH}} \underset{b}{\overset{a}{\rightleftharpoons}} D + 3AH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where M stands for monomer, and D for dimer. In this scheme three molecules of acid are involved in the addition of a proton to the double bond; one molecule acts as a proton donor, and the other two take part in solvating the resulting ion pair. These ions must exist as ion pairs to give the observed kinetic results.

If the rate-controlling step for the forward reaction were reaction (2*a*) then the initial rate of dimerization, as given by the initial slope of the volume decrease–time curve, would be :

$$k_{2a}[(\mathrm{HM^+A^-})_{\mathrm{solv.\ 2AH}}][\mathrm{M}]$$
$$= k_{2a}(k_{1a}/k_{1b})[\mathrm{AH}]^3[\mathrm{M}]^2$$

This is of the same form as that found experimentally, where

$$k_f = k_{2a}(k_{1a}/k_{1b}) = k_{2a} \,.\, K_1$$

Similarly, if the rate-controlling step for the reverse reaction were reaction (2*b*), then the initial rate of the reverse reaction, as given by the initial slope of the volume increase–time curve, would be :

$$k_{2b}[(\mathrm{HD^+A^-})_{\mathrm{solv.\ 2AH}}]$$
$$= k_{2b}(k_{3b}/k_{3a})[\mathrm{AH}]^3[\mathrm{D}]$$

This is of the same form as that found experimentally where

$$k_r = k_{2b}(k_{3b}/k_{3a}) = k_{2b}/K_3$$

Thus, our results are explained by the above mechanism with reactions (2*a*) and (2*b*) as the rate-determining steps for the forward and the reverse reaction respectively. The same order in acid and dimer for the initial rate of the reverse reaction would be obtained if the slow step in the reverse reaction were (3*b*). We do not believe this to be the case, however, as both the forward and the reverse reaction are accompanied by an instantaneous development of colour which we attribute to the establishment of equilibria (1) and (3), since the ion formed by adding a proton to 1 : 1-diphenylethylene is coloured [A. G. Evans and Hamann, *Proc. Roy. Dublin Soc.*, 1950, **25** (N.S.), 139; A. G. Evans, *loc. cit.*].

Velocity Constants eand Equilibrium Constant.—From the dependence of the initial rates of the forward and the reverse reaction on the olefin and acid concentrations, we have established that the order of reaction in the forward direction is 2 in monomer and 3 in acid, and in the reverse direction is 1 in dimer and 3 in acid. From the dependence of the equilibrium concentrations of monomer and dimer on the total amount of olefin present, we have established that the ratio of the orders of reaction in the forward and the reverse direction is 2 : 1 for monomer : dimer, and that both reactions are of the same order in acid. In this respect, then, both the kinetic analysis of the reaction rates and the determination of the equilibrium conditions of the system are in agreement.

Temp.	$10^7 k_f$ * (mole$^{-4\cdot1}$ l.$^{4\cdot1}$ sec.$^{-1}$) (initial slope)	$10^7 k_r$ * (mole$^{-3\cdot1}$ l.$^{3\cdot1}$ sec.$^{-1}$) (initial slope)	$10^7 k_r$ * (mole$^{-3\cdot1}$ l.$^{3\cdot1}$ sec.$^{-1}$) $= k_f/K$	k_f/k_r (mole^{-1} l.)	K (mole^{-1} l.)
33·8°	18·2	4·8	1·15	3·8	15·85
45·7	32·5	13·0	3·78	2·5	8·59
54·7	45·0	27·1	8·04	1·7	5·60

* k_f and k_r are evaluated in terms of the number of moles per l. of dimer appearing and disappearing respectively per sec.

We should expect the ratio of the velocity constants, k_f/k_r, to equal the value of K determined from the equilibrium conditions of the system. It is seen from the Table that the k_f/k_r ratios are lower than the corresponding K values. We believe K to be the more accurate, since the amounts of dimer present at equilibrium, determined (*a*) by weighing, and (*b*) by volume change, agree, as mentioned above, to within 4%. As regards the k_f and k_r values obtained from the initial slopes of the forward and reverse reactions respectively, and given in the Table, we believe the former to be the more accurate. The volume changes associated with the reverse reactions are much smaller than those for the forward reactions, making k_r less reliable than k_f; indeed Figs. 4*a* and 2*a* show that the reproducibility of k_r is much less than that of k_f. Further, we have found that, unless rigorous precautions are taken in purifying the dimer, large initial slopes may be obtained for the reverse reactions although the m. p. of the dimer used is correct. This suggests that, even in the purest samples of dimer we have made, some trace impurity may still remain, which accelerates both the reverse and the forward reactions and does not affect the final equilibrium position. Although the monomer has been purified in several different ways, we have never found any such variation in the values for the initial slope of the forward reaction. We believe, therefore, that the best values of k_r are obtained from the forward reactions, that is, from the ratio k_f/K. The values obtained in this way are given in the Table.

According to our mechanism the equilibrium constant, K, is related to the individual rate constants as follows :

$$K = \frac{k_f}{k_r} = \frac{k_{1a}}{k_{1b}} \cdot \frac{k_{2a}}{k_{2b}} \cdot \frac{k_{3a}}{k_{3b}} = K_1K_2K_3$$

Activation Energies and Heats of Reactions.—The activation energies for the forward and the reverse reaction, obtained from the temperature dependence of the initial slopes and the exothermicity of the dimerisation reaction Q are:

$$E_f = 9{\cdot}1 \text{ kcal. mole}^{-1}. \quad E_r = 17{\cdot}3 \text{ kcal. mole}^{-1}.$$
$$E_r - E_f = 8{\cdot}2 \text{ kcal. mole}^{-1}. \quad Q = 10{\cdot}1 \text{ kcal. mole}^{-1}.$$

The activation energy for the forward reaction, E_f, will be the sum of the endothermicity of reaction (1*a*) and the activation energy of reaction (2*a*). The activation energy for the reverse reaction, E_r, will be the sum of the endothermicity of reaction (3*b*) and the activation energy of reaction (2*b*). The difference of these ($E_r - E_f$), 8·2 kcal./mole, is in fair agreement with the value 10·1 kcal./mole for the exothermicity of the dimerization reaction, Q, obtained from our equilibrium measurements. From the above discussion regarding the accuracy of k_r, we believe that a better value for E_r is given by $(E_f + Q) =$ 19·2 kcal./mole. Although the activation energies are small, the forward and the reverse reactions are extremely slow. This will be so because the transition-state complex involves not only two olefin molecules in special orientation, but also three trichloroacetic acid molecules (in addition to any benzene solvating the complex), and thus the entropy of activation, and hence the temperature-independent factor, will be very small indeed.

It has been shown in earlier work on the polymerization of *iso*butene and methyl methacrylate that the bulky side groups reduce the heat of polymerization below that expected theoretically (A. G. Evans and Tyrrall, *J. Polymer Sci.*, 1947, **2**, 387). In the reaction now studied, the bulky phenyl groups prevent the reaction from proceeding beyond the dimer, and we may thus expect that the exothermicity of reaction, 10·1 kcal./mole, is lower than it otherwise would be because of steric compressions which are present in the dimer but not in the monomer. The extent of this steric hindrance was demonstrated when a model of the dimer was made. Using Courtauld atomic models, which allow some distortion of bonds, it was impossible to make the dimer unless more flexible links were used : even then great difficulty was experienced.

Solvation of Ions.—Our postulate that the trichloroacetic acid acts as a solvent for the ion pairs is justifiable. Acetic acid can solvate ion pairs of the type R^+Cl^- where R is a triarylmethyl group, and this property is more marked than would be expected from the value of the dielectric constant of acetic acid (A. G. Evans, Price, and Thomas, *Trans. Faraday Soc.*, in the press). This ability to act as a solvent for ionization has been demonstrated for trichloroacetic acid (cf. above) since this acid produced ionization of triarylmethyl chlorides in benzene. Further confirmation has been obtained from recent experiments on the dimerization of 1 : 1-diphenylethylene, catalysed by trichloroacetic acid, in nitroethane, which is more polar than benzene. Here we find the forward reaction to be of second order in monomer and of order 2·4 in acid, and the reverse reaction to be of first order in dimer and of order 2·4 in acid. The smaller order in acid is to be expected in this more polar solvent, since nitroethane is quite an efficient solvent for the ionization of triarylmethyl halides (Bentley, A. G. Evans, and Halpern, *Trans. Faraday Soc.*, **1951**, **47**, 711; Bentley and A. G. Evans, *J.*, 1952, 3468), and will thus play a more important part than will benzene in the solvation of the ion pairs formed in the reaction of **1 : 1**-diphenylethylene.

The fact that the catalyst in these reactions not only acts as a proton donor to the olefin, but also takes part in solvating the ions so formed, is of great significance. Thus, in general, quite an appreciable part of the efficiency of a cationic catalyst, especially in solvents of low ionizing power, may be determined by its contribution to the solvation of the ionic intermediates of the reaction.

UNIVERSITY COLLEGE, CARDIFF.

[*Received, January 12th*, 1955.]