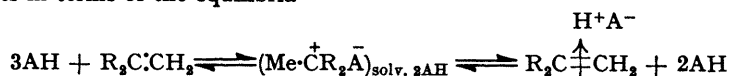


18. *The Activation of Carbon-Carbon Double Bonds by Cationic Catalysts. Part III.*<sup>1</sup> *The Coloured Species formed by the Interaction of 1 : 1-Di-*p*-methoxyphenylethylene with Trichloroacetic Acid in Benzene.*

By ALWYN G. EVANS, PETER M. S. JONES, and J. H. THOMAS.

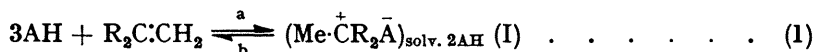
Spectroscopy shows that two coloured species are formed in the 1 : 1-di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene system in the dark, one of which we believe to be the classical carbonium ion, by analogy with the spectrum of this olefin in concentrated sulphuric acid, and the other a  $\pi$ -complex between the acid and the olefinic double bond. We interpret our results in terms of the equilibria



(where R = *p*-MeO·C<sub>6</sub>H<sub>4</sub>·, here and throughout this paper), the first of which is set up much more rapidly than the second. AH is dimeric trichloroacetic acid, and two molecules of acid help in solvating the ion pairs which involve carbonium ions.

IN Part II<sup>1</sup> we studied the dimerization of 1 : 1-di-*p*-methoxyphenylethylene in benzene using trichloroacetic acid as catalyst. Under these conditions an equilibrium mixture of monomer and dimer was obtained. When higher concentrations of acid and lower concentrations of monomer were used, the dimerization to the equilibrium monomer-dimer position occurred instantaneously, and the concentration of dimer present at equilibrium (calculated from the equilibrium constant) was very much smaller than that of the monomer; we are therefore virtually studying the interaction of trichloroacetic acid with 1 : 1-di-*p*-methoxyphenylethylene in benzene in the absence of any complication due to dimerization. Some preliminary results obtained by a spectrophotometric study of such systems were given in Part II.<sup>1</sup> It was found there that the addition of a high concentration of trichloroacetic acid to benzene solutions of 1 : 1-di-*p*-methoxyphenylethylene caused (a) the immediate production of an absorption peak at 498 m $\mu$  which we attributed to the classical carbonium ion (I) formed by proton transfer from the acid AH to the olefin and (b) a second absorption peak at 680 m $\mu$  which developed more slowly and which we attributed to a coloured  $\pi$ -complex.

The dependence of the carbonium-ion concentration on the concentration of acid and olefin showed that the equilibrium involved is :



where two molecules of acid help in solvating the ion pair.

We now give further data for equilibrium (1) and for the production and constitution of the second coloured species which absorbs at 680 m $\mu$ .

#### EXPERIMENTAL AND RESULTS

*Materials.*—Benzene, 1 : 1-di-*p*-methoxyphenylethylene, and trichloroacetic acid were purified as described earlier.<sup>1,2</sup> 3-Methyl-1 : 1 : 3-triphenylindane, prepared and purified by Schoepfle and Ryan's method,<sup>3</sup> had m. p. 142.5°. 1 : 1-Diphenylethane was prepared by Cook and Chambers's method<sup>4</sup> and was fractionated twice under reduced pressure. (We thank Mr. J. Lewis for carrying out this preparation.)

<sup>1</sup> Part II, A. G. Evans, N. Jones, P. M. S. Jones, and J. H. Thomas, *J.*, 1956, 2757.

<sup>2</sup> A. G. Evans, N. Jones, and J. H. Thomas, *J.*, 1954, 1824.

<sup>3</sup> Schoepfle and Ryan, *J. Amer. Chem. Soc.*, 1930, **52**, 4021.

<sup>4</sup> Cook and Chambers, *J. Amer. Chem. Soc.*, 1921, **43**, 336.

"AnalaR" sulphuric acid was used without further purification. "AnalaR" acetic acid was purified as previously outlined.<sup>5</sup>

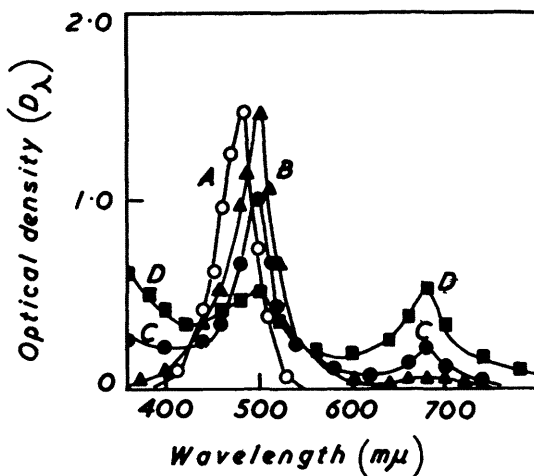
*Procedure.*—Solutions of trichloroacetic acid in benzene<sup>2</sup> and of 1:1-di-*p*-methoxyphenylethylene in benzene, both of known concentration, were made up. Various volumes of these solutions were made up to 10 ml. with benzene in graduated flasks and shaken, and the pink homogeneous solutions were then transferred to Pyrex-glass optical cells of 2 cm. cross-sectional diameter whose opposing faces were optical flats. The cells were filled through a side-arm in the cylindrical surface, the side-arm was sealed off, and the cell left in the dark at room temperature. The spectra of the solutions were measured at known intervals with a Unicam S.P. 500 spectrophotometer until no further change occurred. The optical densities given refer to 1 cm. path length, and the trichloroacetic acid concentrations are expressed in terms of the dimer acid.

1:1-Di-*p*-methoxyphenylethylene-Acid-Benzene Systems.—*Experimental conditions.* The concentration of olefin used, measured as monomer, was  $10^{-3}$ – $10^{-4}$  mole  $l^{-1}$ . The concentration of dimer present, due to the monomer-dimer equilibrium which is set up immediately at these high acid concentrations, was  $10^{-5}$ – $10^{-7}$  mole  $l^{-1}$  respectively, as calculated from our monomer-dimer equilibrium constant.<sup>1</sup> Thus we can assume (as in Part II) that in these conditions all the olefin present may be taken as monomer, since the olefin is always at least 99% monomer.

FIG. 1. Absorption spectra for the 1:1-di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene system.

A; 1:1-Di-*p*-methoxyphenylethylene ( $2.66 \times 10^{-5}$  mole  $l^{-1}$ ) in 98%  $H_2SO_4$ .

B, C, D; 1:1-Di-*p*-methoxyphenylethylene ( $1.33 \times 10^{-4}$  mole  $l^{-1}$ ) and trichloroacetic acid ( $2.00$  mole  $l^{-1}$ ) in benzene at 20° after: B, 20 min.; C, 47 hr.; D, 250 hr. (after this no further change in spectrum occurred).



*Spectra.* A typical result for the change of spectrum with time is given in Fig. 1 (Curves B, C, and D) for a solution of high acid concentration; the 498  $m\mu$  peak develops immediately and this is followed by the slow development of the 680  $m\mu$  peak. The 498  $m\mu$  peak falls as the 680  $m\mu$  peak approaches its equilibrium value.

It is seen from Fig. 1 that the optical density of the solution rises as the wavelength decreases below 420  $m\mu$ . This leads to a large ultraviolet peak at about 320  $m\mu$  which overlaps with the olefin absorption peak at 295  $m\mu$  and the second peak of the carbonium-ion spectrum (given by the olefin in concentrated sulphuric acid) at 330  $m\mu$ . This overlap prevents the quantitative measurement of the 320  $m\mu$  peak, although we have found that at low olefin concentrations ( $\sim 10^{-4}$  mole  $l^{-1}$ ) the optical density at 360  $m\mu$  (an arbitrary point on the visible edge of this absorption peak where little interference will occur) is directly proportional to the height of the 680  $m\mu$  peak (as can be seen in Fig. 1), indicating that the same species is absorbing in both the ultraviolet and the 680  $m\mu$  region. (This inference is supported by work on other olefins, to be published.) The quantitative results presented here for this species have been obtained from measurements on the 680  $m\mu$  peak where no interference due to other species occurs.

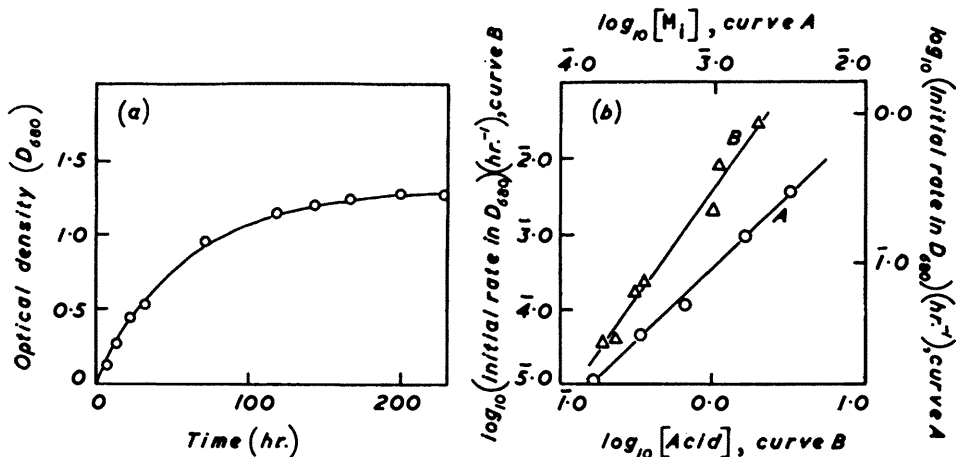
*Equilibrium concentration of carbonium ions.* In Part II we took the  $\int D_{\lambda} d\lambda$  of the 498  $m\mu$  peak as a measure of the concentration of the monomer ions in these solutions. This we claimed was justified since (a) the spectrum is so similar to that of the olefin in concentrated sulphuric acid, and (b) in this very dilute olefin solution the concentration of dimer is so much smaller

<sup>5</sup> A. G. Evans, Price, and J. H. Thomas, *Trans. Faraday Soc.*, 1955, **51**, 481.

than that of the monomer. By measuring the concentration of carbonium ions immediately the system was made up we showed that it was determined according to equilibrium (1), and the values of the equilibrium constant  $K_1$  ( $3.1 \times 10^{-3}$  mole $^{-2}$  l. $^2$ ), the increase in heat content  $\Delta H_{1a}^\circ$  ( $-3.5$  kcal. mole $^{-1}$ ), and the increase in entropy  $\Delta S_{1a}^\circ$  ( $-19$  cal. deg. $^{-1}$  mole $^{-1}$ ) were obtained for this reaction. We have extended the measurements on  $K_1$  and give the mean values for  $K_1$ ,  $\Delta G_{1a}^\circ$  and  $\Delta S_{1a}^\circ$  in Tables 1 and 2. It is seen that the results given in Part II are completely confirmed by this more detailed investigation.

*Rate of production of the 680 m $\mu$  species.* A typical plot of  $D_{680}$ , the optical density at 680 m $\mu$ , against time is given in Fig. 2a. These are smooth curves which reach a maximum value of  $D_{680}$  after which no further change with time is observed during several months. A measure of

FIG. 2. Rate of development of the 680 m $\mu$  species in the 1 : 1-di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene system at 20 $^\circ$ .



(a) Trichloroacetic acid (1.11 mole l. $^{-1}$ ) and 1 : 1-di-*p*-methoxyphenylethylene ( $3.3 \times 10^{-4}$  mole l. $^{-1}$ ) in benzene at 20.0 $^\circ$ .

(b) Orders in acid and olefin for the initial rate of production of the 680 m $\mu$  species.

A; Constant trichloroacetic acid concentration (1.18 mole l. $^{-1}$ ) at 20.0 $^\circ$ . Slope (order in olefin) =  $1.0 \pm 0.2$ . The olefin concentrations used on this plot are those obtained after correcting for the carbonium-ion concentration.

B; After the amount of olefin converted into carbonium ion has been allowed for, all points have been scaled to a constant  $1.33 \times 10^{-4}$  mole l. $^{-1}$  of 1 : 1-di-*p*-methoxyphenylethylene by using the first-order dependence of rate of development of 680 m $\mu$  peak on the olefin concentration found in curve A. Slope (order in acid) =  $2.9 \pm 0.2$ . Temp. = 20.0 $^\circ$ .

TABLE 1. 1 : 1-Di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene.

Species	Rate of formation (order)		Equilibrium concn. (order)	
	Acid	Olefin	Acid	Olefin
Classical ion .....	$2.8 \pm 0.2$ *	$1.0 \pm 0.2$ *	$2.8 \pm 0.2$	$1.0 \pm 0.2$
680 m $\mu$ $\pi$ -complex .....	$2.9 \pm 0.2$	$1.0 \pm 0.2$	$1.0 \pm 0.2$	$1.0 \pm 0.2$

\* These values are obtained by dilatometric work given in Part II.

TABLE 2. Thermodynamic constants for reactions in the 1 : 1-di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene system.

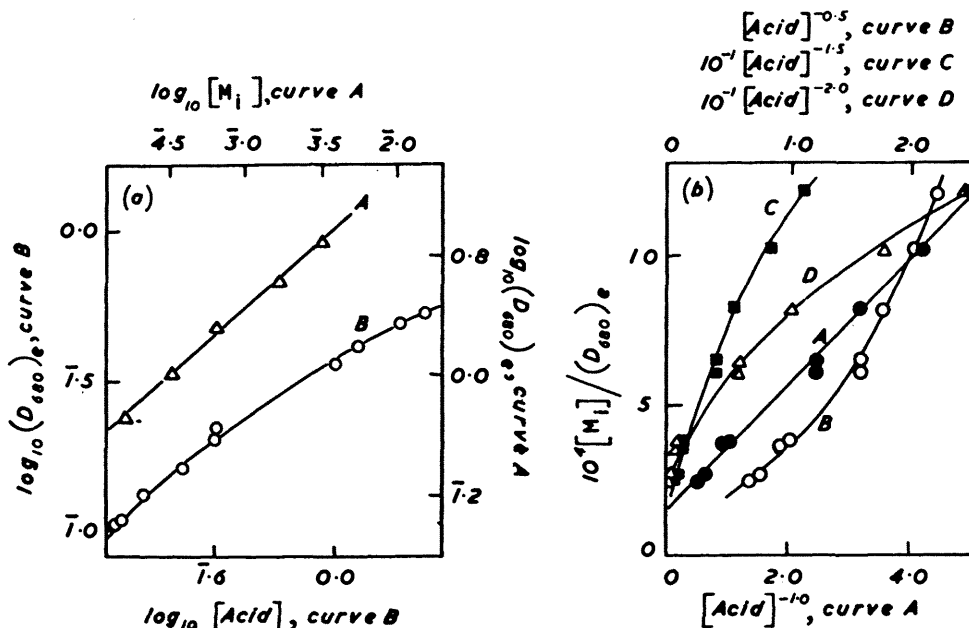
Species	$K$ (20 $^\circ$ )	$\Delta G^\circ$ (20 $^\circ$ ) (kcal. mole $^{-1}$ )	$-\Delta H^\circ$ * (kcal. mole $^{-1}$ )	$-\Delta S^\circ$ (20 $^\circ$ ) (cal. mole $^{-1}$ deg. $^{-1}$ )
Classical ion	$K_1 = 3.6 \times 10^{-3}$ mole $^{-2}$ l. $^2$	$\Delta G^\circ_{1,a} = 1.9 \pm 0.2$	$-\Delta H^\circ_{1,a} = 3.5 \pm 0.2$	$-\Delta S^\circ_{1,a} = 19 \pm 2$
680 m $\mu$ $\pi$ -complex	$K_{680} = K_1 K_4 = 7.1 \times 10^{-1}$ mole $^{-1}$ l.	$\Delta G^\circ_{680} = \Delta G^\circ_{1,a} + \Delta G^\circ_{4,a} = 0.2 \pm 0.2$	—	—

The values of  $K$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$  are calculated by using the mole l. $^{-1}$  as the standard state.

\* This value is taken from Part II.

the initial rate of production of the 680  $\mu$  species was obtained by drawing tangents to the curves at zero time. Initial rates were found in this way for different initial total olefin concentrations at constant initial acid concentrations, and the plot of  $\log_{10}$  (initial rate) against  $\log_{10} [M_i]$  is given in Fig. 2b, curve A, where  $M_i$  is the initial olefin taken as monomer corrected for the loss of monomer according to the instantaneously established equilibrium (1). This correction to the monomer concentration was 5.6%. The slope of this plot is  $1.0 \pm 0.2$ , showing that the rate of formation of the 680  $\mu$  species is of the first order in olefin. Initial rates were also found in the same way for a series of runs at varying acid concentrations for constant initial olefin concentration. The fact that olefin is removed instantaneously according to equilibrium (1) was allowed for by using  $K_1$  and correcting the rate on the basis of the first-order dependence on monomer found above. This correction is of the order of 23% for the highest acid concentration but rapidly becomes negligible as the acid concentration is reduced. The plot of  $\log_{10}$  (initial rate) against  $\log_{10}$  (initial acid concentration) is given in Fig. 2b, curve B, whose slope is

FIG. 3. Equilibrium concentrations of the 680  $\mu$  species at 20°.



(a) Variation with acid and olefin concentration.

A; Constant trichloroacetic acid concn. ( $1.18 \text{ mole l}^{-1}$ ) at  $20.0^\circ$ . Slope (order in olefin) =  $1.0 \pm 0.2$ . The olefin concentrations used in this plot are those obtained after correction for the carbonium-ion concentration.

B; After the amount of olefin converted into carbonium ion had been allowed for, all points have been scaled to a constant  $1.33 \times 10^{-4} \text{ mole l}^{-1}$  of 1:1-di-*p*-methoxyphenylethylene, by using the first-order dependence of  $(D_{680})_0$  on olefin concentration found in curve A.

(b) Determination of order in acid. All points have been corrected for the carbonium-ion concentration as for curve A, Fig. 3(a).

Curve A is for unit order in acid. Curves B, C, and D are those for assumed acid orders of 0.5, 1.5, and 2.0 respectively. From intercept of curve A,  $\epsilon_{680} = 6.7 \times 10^3$ , and from slope of curve A,  $K_{680} = 0.71 \text{ mole}^{-1} \text{ l}$ .

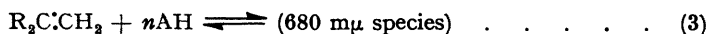
$2.9 \pm 0.2$ , showing that the order in acid for the formation of the 680  $\mu$  species may be taken as 3. We can express these results as follows :

$$\text{Rate of formation of 680 } \mu \text{ species} = k_{680} [R_2C^+CH_2] [AH]^3 \quad (2)$$

where  $k_{680}$  is the velocity constant for the production of this species.

The equilibrium concentrations for the 680  $\mu$  species. It is found that the optical density of the 680  $\mu$  species at equilibrium,  $(D_{680})_0$  (which we take as directly proportional to the

equilibrium concentration of this species), depends on both the acid and the olefin concentration. In Fig. 3a, curve A, the plot of  $\log_{10} (D_{680})_e$  against  $\log_{10} [M]$  at constant initial acid concentration is a straight line of slope  $1.0 \pm 0.2$ . In Fig. 3a, curve B, the plot of  $\log_{10} (D_{680})_e$  against  $\log_{10}$  (acid concentration) at constant initial olefin concentration corrected as above appears to be a curve. This apparent change in acid order could arise if the equilibrium producing the 680 m $\mu$  species:



lay well to the right. To test this the Benesi-Hildebrand<sup>6</sup> plot was made and the plots of  $[M]/(D_{680})_e$  against  $1/[AH]^n$  are given in Fig. 3b for  $n = 0.5, 1.0, 1.5,$  and  $2.0$ . The value of  $n$  which gives the best straight line is unity (Fig. 3b, Curve A).

Thus the equation which best represents the equilibrium formation of the 680 m $\mu$  species is (3;  $n = 1$ ). Further we see that, although the monomer concentration varies over a 10-fold range, the points lie very well on the straight line, thus confirming the first-order dependence on monomer.

From this plot the intercept on the  $[M]/(D_{680})_e$  axis is  $1/\epsilon_{680}$  and the slope is  $1/(K_{680} \times \epsilon_{680})$  where  $K_{680}$  is the equilibrium constant of equation (3;  $n = 1$ ) and  $\epsilon_{680}$  is the extinction coefficient at 680 m $\mu$  of the 680 m $\mu$  species. The value of  $\epsilon_{680}$  so obtained is  $6.7 \times 10^3$  and the value of  $K_{680}$  is  $7.1 \times 10^{-1} \text{ mole}^{-1}$ .

The fact that the production of the 680 m $\mu$  species depends on a lower order in acid than does that of the classical carbonium ion was expected, in that a reduction of the acid concentration of the equilibrium solutions results in a greater drop in the 498 m $\mu$  peak than in the 680 m $\mu$  peak. For systems of the type shown in Fig. 1, in which the 498 m $\mu$  peak decreases as the 680 m $\mu$  peak increases, it is found, by using  $\epsilon_{680}$  to calculate the amount of olefin converted into the 680 m $\mu$  species, that at all stages the concentration of the carbonium ions is related to that of the unchanged olefin by the equilibrium constant  $K_1$ . Thus the rate of formation of the 680 m $\mu$  species is not fast enough to upset the instantaneous establishment of equilibrium (1).

*Recovery of materials.* 1 : 1-Di-*p*-methoxyphenylethylene (0.18 g.) in a benzene solution of trichloroacetic acid (0.96 mole  $l^{-1}$ ) (10.0 ml.) was allowed to attain equilibrium. In these conditions 37% of the monomer would be converted into the 680 m $\mu$  species. This solution was titrated with sodium hydroxide solution, and the results showed that no acid had been irreversibly removed. The solution was then washed with water, and the organic layer separated. This was evaporated at room temperature under high vacuum, and the resultant oil weighed. A small portion of this was made up to a known concentration in concentrated sulphuric acid, and its absorption spectrum measured. The spectrum was the same as that of a solution of pure 1 : 1-di-*p*-methoxyphenylethylene in concentrated sulphuric acid, and, the extinction coefficient of the classical ion formed in this solution being known, the amount of monomer olefin present could be calculated. In this way it was found that all the material in the solution was 1 : 1-di-*p*-methoxyphenylethylene, showing that no olefin had been irreversibly removed.

*Other Olefin-Acid-Solvent Systems.*—The 1 : 1-Diphenylethylene-Trichloroacetic Acid-Benzene System.—The monomer gave the spectrum in concentrated sulphuric acid shown in Curve A, Fig. 4. The peak at 425 m $\mu$  is due to the complete conversion into the monomer ion  $^+Ph_2C-CH_3$ . When trichloroacetic acid is added to benzene solution of the monomer the spectra shown in Fig. 4, curves D and E, are obtained. These spectra show a peak at 607 m $\mu$  which develops slowly. Unlike the case of 1 : 1-di-*p*-methoxyphenylethylene, only one peak develops under these conditions in the visible region.

To tell whether or not this peak at 607 m $\mu$  is due to the interaction of the acid with the olefin double bond, 1 : 1-diphenylethane was added to a benzene solution of trichloroacetic acid to give a solution of comparable concentration to that used for 1 : 1-diphenylethylene. No absorption in the visible region occurred in this system, showing that the spectrum obtained above must have been due to the interaction of trichloroacetic acid with the olefin double bond.

To determine whether the spectrum was that of the classical carbonium ion modified by a change in medium, we examined the spectra of this 1 : 1-diphenylethylene in various sulphuric acid-acetic acid mixtures (see Fig. 4, curves B and C). We find that under these conditions

<sup>6</sup> Benesi and Hildebrand, *J. Amer. Chem. Soc.*, 1948, **70**, 2832; 1949, **71**, 2703.

<sup>7</sup> A. G. Evans and Hamann, *Sci. Proc. Roy. Dublin Soc.*, 1950, **25**, 1939; A. G. Evans, *J. Appl. Chem.*, 1951, **1**, 240.

there are in general two absorption peaks, one at 430  $m\mu$  corresponding to that found in pure concentrated sulphuric acid (Fig. 4, Curve A) and one at 607  $m\mu$  corresponding to the peak found in our trichloroacetic acid-olefin-benzene systems. In curve C it is seen that the optical density rises rapidly below 400  $m\mu$ . We therefore conclude that the 607  $m\mu$  peak in these systems is due to the same type of coloured species as that of the 680  $m\mu$  species in the 1 : 1-di-*p*-methoxyphenylethylene-acid-benzene systems, the spectrum of which also rises at wavelengths below 420  $m\mu$  (Fig. 1). Further, for 1 : 1-di-*p*-methoxyphenylethylene in concentrated sulphuric acid-acetic acid two peaks develop, at 489  $m\mu$  and at 680  $m\mu$ . Thus, it is clear that 1 : 1-diphenylethylene can behave in the same way as does 1 : 1-di-*p*-methoxyphenylethylene in producing two distinct coloured species by interaction with acids.

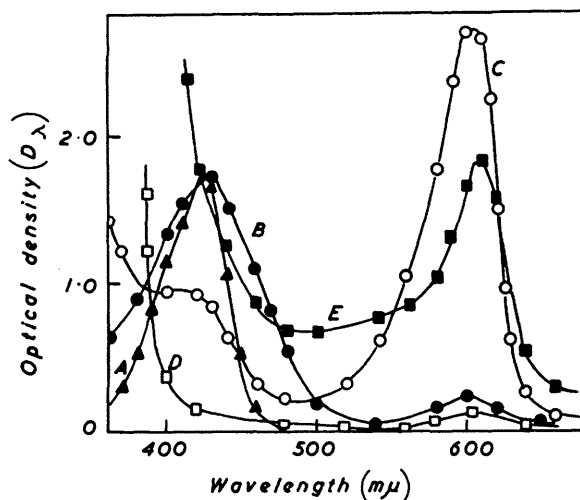


FIG. 4. Absorption spectra for acid solutions of 1 : 1-diphenylethylene in the dark at 16.9°.

A,  $6.8 \times 10^{-2}$  mole  $l^{-1}$  in 98%  $H_2SO_4$ .  
 B,  $4.4 \times 10^{-4}$  mole  $l^{-1}$  and  $H_2SO_4$  (13.9 moles  $l^{-1}$ ) in acetic acid after 5 min.  
 C,  $2.2 \times 10^{-2}$  mole  $l^{-1}$  and  $H_2SO_4$  (7.9 moles  $l^{-1}$ ) in acetic acid after 5 min.  
 D, 1.11 moles  $l^{-1}$  and trichloroacetic acid (1.86 moles  $l^{-1}$ ) in benzene after 20 min.  
 E, As D, after 70 hr.

In certain circumstances 1 : 1-diphenylethylene dimerises to 3-methyl-1 : 1 : 3-triphenylindane.<sup>3</sup> This non-olefinic dimer is not formed in the trichloroacetic acid-catalysed dimerisation reported in Parts I<sup>2</sup> and II.<sup>1</sup> A solution was made containing 0.169 mole  $l^{-1}$  of 3-methyl-1 : 1 : 3-triphenylindane together with 1.92 moles  $l^{-1}$  of trichloroacetic acid in benzene. This was kept in a sealed tube at room temperature, and it was found that no colour developed during several months.

*Other olefins.* Various 1 : 1-diarylethylenes and tetra-arylethylenes give peaks in the 600—800  $m\mu$  region, together with a peak or shoulder in the region 425—500  $m\mu$  (corresponding to the

TABLE 3. Visible absorption peaks appearing in olefin-acid systems.

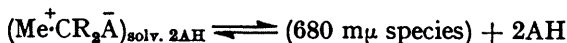
Olefin	Medium	Visible absorption max. ( $m\mu$ )	Ref.
$Ph_2C:CH_2$ .....	Conc. $H_2SO_4$	425	a
	Conc. $H_2SO_4-CH_3-CO_2H$	430, 607	b (Fig. 4)
	$C_6H_5-CCl_3-CO_2H$	607	b (Fig. 4)
<i>(p</i> -Me- $C_6H_4$ ) $_2C:CH_2$ .....	Conc. $H_2SO_4$	455	c
	$C_6H_5-CCl_3-CO_2H$	460, 637	c
$R_2C:CH_2$ .....	Conc. $H_2SO_4$	487	b (Fig. 1)
	$C_6H_5-CCl_3-CO_2H$	498, 680	b (Fig. 1)
	Conc. $H_2SO_4-CH_3-CO_2H$	489, 680	b
$Ph_2C:CPh_2$ .....	$C_6H_5-CCl_3-CO_2H$	425, 445, 680	c
	$Ph \cdot NO_2-CCl_3-CO_2H$	450, 680	c

a Ref. 7. b Present work. c Evans, Jones, and Thomas, unpublished work.

classical carbonium-ion peak produced in concentrated sulphuric acid solution) when in solution with an acid weaker than sulphuric acid. We are studying these peaks quantitatively. Table 3 gives the positions of the visible absorption peaks for some of the systems already studied.

## DISCUSSION

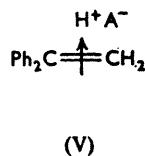
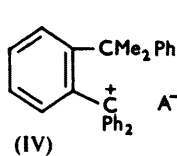
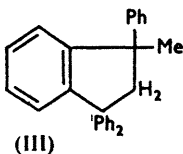
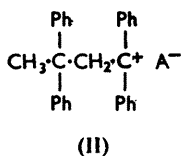
*The 1:1-Di-p-methoxyphenylethylene-Acid-Benzene System.*—Of the two species formed by trichloroacetic acid and 1:1-di-*p*-methoxyphenylethylene in the dark, one is the classical ion with an absorption peak at 498 m $\mu$  formed according to equation (1, a), and the other has an absorption peak at 680 m $\mu$  and is formed by a reaction whose rate-determining step is of order 3 in acid and 1 in total initial olefin. This species must be due to the interaction of the acid with the olefin double bond since it does not occur when the corresponding ethane is used; <sup>1</sup> it is suggested that this species is produced from the classical carbonium ion by a proton rearrangement accompanied by a loss of two acid molecules from the solvation shell:



Since the 680 m $\mu$  peak develops so much more slowly than does the 498 m $\mu$  peak, the establishment of this equilibrium must be much slower than that for the production of carbonium ions.

*The 1:1-Diphenylethylene-Acid-Benzene System.*—This olefin behaves similarly to 1:1-di-*p*-methoxyphenylethylene in that in some solutions of weaker acidity than concentrated sulphuric acid, *e.g.*, sulphuric acid-acetic acid systems, two coloured species are formed, one having the same spectrum as that obtained in concentrated sulphuric acid, and thus being the classical carbonium ion, and the other having an absorption in the 600 m $\mu$  region.

*The Nature of the Coloured Species (600—680 m $\mu$  Region).*—In Part II we suggested that this species was a  $\pi$ -complex, since it was shown to be definitely associated with the interaction of the acid and the olefin double bond. An alternative possibility is that the interaction of the acid with the olefin double bond leads to a coloured classical carbonium ion different from that obtained in concentrated sulphuric acid solution, or to a non-ionic

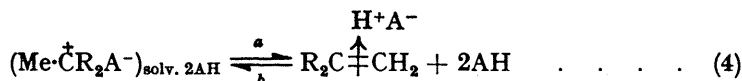


molecule having an absorption in the 600—680 m $\mu$  region. For 1:1-diphenylethylene there are three possible alternative species. The but-1-ene dimer ion (II) cannot be the cause of the 600—680 m $\mu$  peak since 1:1-diphenylethylene in trichloroacetic acid-benzene gives the peak before any appreciable dimerization has occurred, and its height decreases as the dimerization to 1:1:3:3-tetraphenylbut-1-ene proceeds.

The indane dimer of 1:1-diphenylethylene (III) gives no colour in trichloroacetic acid-benzene solutions. Hence neither the indane nor products formed from it, *e.g.*, (IV), can be responsible for this spectrum.

We are left therefore with only the  $\pi$ -complex (V) as a possible structure for the 607 m $\mu$  species, the olefin double bond acting as an electron donor and the acid proton as acceptor. Further, in view of the similar behaviour of the two olefins, we also postulate a  $\pi$ -complex structure for the 680 m $\mu$  species formed in the 1:1-di-*p*-methoxyphenylethylene-trichloroacetic acid-benzene systems.

*The  $\pi$ -Complex of 1:1-Di-p-methoxyphenylethylene.*—The formation of the 680 m $\mu$  complex will occur according to the equation (4). If the carbonium ion equilibrium is set up



rapidly and the  $\pi$ -complex equilibrium more slowly, the velocity constant  $k_{680}$  (eqn. 2) will be equal to the product of the velocity constant of reaction (4, a) and the equilibrium constant of reaction (1), *i.e.*,  $k_{680} = k_{4,a} \cdot K_1$ . Further, the equilibrium constant  $K_{680}$  of reaction (3;  $n = 1$ ) will equal the product of the equilibrium constants of reactions (4) and (1), *i.e.*,  $K_{680} = K_1 K_4$ .

*Rate of formation of the  $\pi$ -complex.* By use of the extinction coefficient  $\epsilon_{680}$  for the  $\pi$ -complex (from Fig. 3b) and the data given in Fig. 2b,  $k_{680}$  can be found, by substitution in equation (2), to be  $1.5 \times 10^{-6}$  mole<sup>-3</sup> l.<sup>3</sup> sec.<sup>-1</sup> at 20°. We have already found  $K_1$  (Table 2) and hence  $k_{4,a} = 4.0 \times 10^{-5}$  sec.<sup>-1</sup>.

The rate constant for the dimerization<sup>1</sup> of 1 : 1-di-*p*-methoxyphenylethylene,  $k_t$ , at 20°, calculated from the results at higher temperatures, would be  $2.1 \times 10^{-1}$  mole<sup>-3</sup> l.<sup>3</sup> sec.<sup>-1</sup>. This is very much greater than  $k_{680}$  and hence the  $\pi$ -complex cannot be the reaction intermediate for the dimerization. For this olefin, therefore, the rate constant of the dimerization,  $k_t$ , which is equal to the rate constant of formation of the reaction intermediate, must be the rate constant of formation of the classical ion,  $k_{1,a}$ , as suggested in Part II.<sup>1</sup>

*Equilibrium constant for the  $\pi$ -complex.* Although the  $\pi$ -complex is formed more slowly than the classical ion, its equilibrium concentration is always greater than that of the classical carbonium ion in the solutions we have used. Since  $K_{680}$  found for the 680 m $\mu$  complex is equal to  $K_1 K_4$ ,  $K_4$  is found to be  $1.87 \times 10$  mole<sup>2</sup> l.<sup>-2</sup>, the value of  $K_1$  given in Table 2 being used.

*Comparison with earlier work.* Our work agrees with that of Maas, Russel, and Wright,<sup>8</sup> who showed that 1 : 1 complexes are formed between acids and olefins, as demonstrated cryoscopically. For the acid-catalyzed hydration of *isobutene*, Taft, Purlee, Reitz, and DeFazio<sup>9</sup> have suggested that a 1 : 1  $\pi$ -complex is first formed, and that this is followed by a slow rate-determining isomerization of the  $\pi$ -complex to the classical ion. Our work, however, shows that for 1 : 1-di-*p*-methoxyphenylethylene the classical ion is formed first, and that this slowly isomerizes to the  $\pi$ -complex. The reactive intermediate in the dimerization of 1 : 1-di-*p*-methoxyphenylethylene is found to be the classical carbonium ion, and this is in agreement with the mechanism of Taft *et al.* for the hydration of *isobutene*.

*Solutions in Daylight.*—All the results presented in this paper have been obtained for solutions kept in the dark. Solutions of 1 : 1-di-*p*-methoxyphenylethylene in daylight develop, in addition to the 680 m $\mu$  peak, one at 620 m $\mu$  which does not develop at all in the dark, and whose rate of formation is very sensitive to the light intensity. The 620 m $\mu$  species is being investigated separately. We also find that although the 680 m $\mu$  species is produced from this olefin in the absence of light, its rate of formation is greater when the solution is illuminated. The 1 : 1-diphenylethylene-trichloroacetic acid-benzene systems also develop an additional peak in the visible region when exposed to light.

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<sup>8</sup> Maas and Russel, *J. Amer. Chem. Soc.*, 1918, **40**, 1561; 1921, **43**, 1227; Maas and Wright, *ibid.*, 1924, **46**, 2664.

<sup>9</sup> Taft, Purlee, Reitz, and DeFazio, *ibid.*, 1955, **77**, 1584.