643. *Catalysis of Diels–Alder Diene Associations. Part V.* Proton- and Electron-transfer Processes.*

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General acid catalysis operates in two typical Diels–Alder associations, *viz.*, (1) the addition of *cyclo*pentadiene to benzoquinone and (2) the dimerisation of *cyclo*pentadiene. The kinetics of these reactions, of the type two substrates + catalyst ⟶ product, make it probable that a proton transfer, involving the transient formation of ion pairs, plays a rôle. The conclusion is based, *inter alia*, on experiments showing that in the presence of some acids diene synthesis (2) is kinetically of the first order with respect to the substrate, and that the rate of both catalysed associations is decreased on addition of relatively small quantities of various substances.

Reaction (1) is catalysed also by phenols; the kinetics and other observations, *e.g.*, the formation of relatively deeply coloured catalyst–substrate complexes, are compatible with the assumption that these processes are initiated by an electron transfer from the phenol to the benzoquinone. Numerical relationships between the catalytic velocity coefficients and the dissociation constants of the catalysts, or between the activation energies and the non-exponential factors of the rate expressions, can be brought into accord with the suggested mechanism both in the acid and in the phenol catalysis. Solvent and temperature effects have been studied, and an estimation could be made of the kinetic parameters characterising bimolecular steps of the over-all reaction.

It has been shown (Part I *) that Diels–Alder diene associations are catalysed by a number of acids and by phenol. An attempt is now made to elucidate the mechanism of this catalysis, the following 1 : 2–1 : 4-additions being chosen for the investigation :

Benzoquinone + *cyclo*Pentadiene = *cyclo*Pentadiene–benzoquinone . . . . (1)
2 *cyclo*Pentadiene = Di*cyclo*pentadiene . . . . (2)

Reaction (1) is the prototype of diene syntheses which lead to strongly polar molecules (see Part III), and reaction (2) represents the alternative type involving hydrocarbons only.

Diene synthesis (1) is catalysed both by acids and by phenols, but (2) is catalysed by acids only : esters, phenol ethers, or bases of various types are inactive. Trichloroacetic acid has been selected for a relatively comprehensive study of the kinetics in various solvents and in the presence of retarders, because this acid has particularly favourable solubility properties and a relatively high catalytic power. Thirty-eight other substances were also tested but an extensive kinetic investigation was not made in each case.

Experimental.

General Remarks.—The mode of purification of the reactants has been described in *J.*, 1935, 828, and the purity of solvents, catalysts, etc., was checked by b. p., m. p., or equivalent-weight determinations.

Simultaneous or consecutive reactions do not play a rôle. This follows not only from the kinetics but also from the almost quantitative conversion of the reactants into *cyclo*pentadiene–benzoquinone or di*cyclo*pentadiene; these substances were isolated by means of a technique described in Part I and

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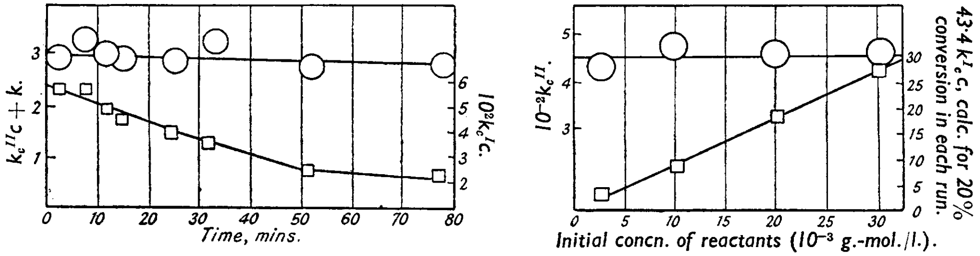
* Parts I—III : Wassermann, *J.*, 1942, 618, 623; 1946, 1089. Part IV: Khambata and Wassermann, *J.*, 1946, 1090.

on p. 3052. The ratio, rate of reaction (1)/rate of reaction (2), was always so large that the dimerisation of *cyclo*pentadiene did not interfere with the other diene addition. The kinetics of (1) were measured colorimetrically (see Part I). In the various runs the results of which are in the third to the eighth section of the right-hand side of Table I, control measurements had to be done in order to determine the initial light absorption of the reaction mixture and to test the validity of Beer's law; this was necessary owing to the formation of coloured complexes between benzoquinone and phenols. No such coloration was observed with the various acids or with *o*-nitrophenol.

The catalytic rate of reaction (2) was measured dilatometrically. Freshly prepared solutions were filled into dilatometers, which had been cooled and evacuated in some runs, and were sealed off as soon as possible. A special apparatus was constructed which enabled one to titrate and fill solutions of hydrochloric or hydrobromic acid in carbon tetrachloride into the dilatometers, without exposing these solutions to atmospheric moisture and without loss of the volatile catalysts. The dilatometric technique was tested, in the first instance, by estimating the velocity coefficients of the uncatalysed reaction (2). The final volume contraction was calculated from the results obtained in control experiments in which a di*cyclo*pentadiene solution of appropriate concentration was filled into the same dilatometer as that used for rate measurements. The velocity constants estimated dilatometrically agreed with those previously determined by a different technique (*J.*, 1936, 1029; 1939, 381).

FIG. 1.

Trichloroacetic acid catalysis of the formation of cyclo*pentadiene–benzoquinone in carbon tetrachloride solution at* 17°.



Circles : left ordinate ; these graphs show that equation (5) *applies. Squares : right ordinate ; these graphs show that equation* (6) *does not apply.*

Left-hand figure : Results of a typical experiment ; a *and* c, *respectively,* 0·0200 *and* 0·00500 *g.-mol./l. The time scale covers the stage up to* 80% *conversion ;* k = 0·24 *l.g.-mol.*$^{-1}$ *min.*$^{-1}$.

Right-hand figure : Each circle is the result of measurements similar to those represented by the left-hand figure. The third circle from the left represents the results of four experiments in which the catalyst concentration was varied in the range 0·00250—0·0100 *g.-mol./l.*

Calculation of Velocity Coefficients.—From a kinetic point of view the reactions here considered have to be divided into two groups. (*a*) The catalysed addition of *cyclo*pentadiene to benzoquinone and the naphthalene-2-sulphonic acid-catalysed dimerisation of *cyclo*pentadiene, the rate of which can be represented by

$$\mathrm{d}x/\mathrm{d}t = k(a - x)^2 + k_c^{II}c(a - x)^2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

(*b*) The dimerisation of *cyclo*pentadiene catalysed by hydrochloric, by tri-, di-, and mono-chloroacetic and by acetic acids, the velocity of these processes being given by

$$\mathrm{d}x/\mathrm{d}t = k(a - x)^2 + k_c^{I}c(a - x) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

In these equations a and $(a - x)$ are the equimolar concentrations of the reactants at zero time and time t, respectively, c is the concentration of the catalyst, k is the rate constant of the bimolecular association known in most cases from previous work, and k_c^{II} and k_c^{I} are the catalytic velocity coefficients, the superscripts referring to the fact that the catalysis is either of the second or of the first order in the substrate. On integration of (3) and (4) one obtains

$$k_c^{II} = \frac{x}{atc(a - x)} - \frac{k}{c} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

$$k_c^{I} = \frac{2{\cdot}30}{tc}\left\{\log_{10}\frac{a}{(a - x)} - \log_{10}\frac{ka + k_c^{I}c}{k(a - x) + k_c^{I}c}\right\} \quad . \; . \; . \; . \; . \; . \quad (6)$$

If the temperature is low or if the conversion is small the last term of (6) can be neglected and in this case k_c^{I} can be calculated as in first-order reactions. If, on the other hand, the last term had to be taken into account, the catalytic velocity coefficient was estimated by a method of successive approximations.

The accuracy of the catalytic velocity coefficients is specified in Tables I and III, the experimental errors depending, *inter alia*, on the difference between $k_c^{II}c$ and k, and on that between the first and the second term of (6). Typical numerical values indicating the magnitude of these differences and showing that the rates of the non-catalysed associations are relatively small are given in Figs. 1 and 5 and on p. 3052. It is not possible, of course, to reconcile the kinetics of the reactions (*a*) with (6) or those of the reactions (*b*) with (5). This is illustrated by typical results, *viz.*, by the graphs relating to the right ordinates of Figs. 1 and 5. The catalytic rate of all the processes here considered [reactions (*a*) and (*b*)] is of the first order with respect to the acid or the phenol. The catalyst concentration was calculated both from the weight of the added catalyst and from the results of alkalimetric titrations made with aliquots of the reaction mixture at various time intervals. The agreement between the two methods was satisfactory in all experiments relating to association (1) and in those runs of reaction (2) which were done in the presence of acetic, chloroacetic, dichloroacetic, and naphthalene-2-sulphonic acids. A similar agreement was obtained in experiments with trichloroacetic acid provided the concentration

TABLE I.

Acid and phenol catalysis of the formation of cyclo*pentadiene–benzoquinone.*

[All k_c^{II} values are in l.^{2} g.-mol.$^{-2}$ min.$^{-1}$ deduced from (5). The k values in chloroform, ether, acetone, and dioxan solution, at 20°, are 2·4, 0·09, 0·54, and 5·0 l. g.-mol.$^{-1}$ min.$^{-1}$.]

Catalyst.	Solvent.	Temp.	$k_c^{\mathrm{II}} \times 10^{-2}$.
$CCl_3\cdot CO_2H$	C_6H_{14}	4°	1·9±0·2 *
		25	2·3±0·2 *
		59	3·5±0·3 *
	C_6H_6	25	1·9±0·2 *
	CCl_4	2	4·8±0·8
		16—20	4·0±0·5
		46	4·4±0·8
	$CHCl_3$	16	0·40±0·08 *
	EtOH	5	<0·2
	Et_2O	20	<0·01
	$COMe_2$	20	<0·002
	$C_4H_8O_2$ †	20	<0·05
$CHCl_2\cdot CO_2H$	CCl_4	2	0·35±0·03
		14—16	0·78±0·05
		37	0·91±0·07
		48	1·1±0·06
	EtOH	20	0·2±0·1
$CH_2Cl\cdot CO_2H$	CCl_4	2	0·08±0·01
		14	0·11±0·01
		37	0·15±0·03
		55	0·20±0·08
	EtOH	20	0·2±0·1
$CH_3\cdot CO_2H$	CCl_4	2	0·0027± 0·0005
		16—20	0·0050± 0·0005
		55	0·025±0·003
	EtOH	20	0·2±0·1
$C_{10}H_7\cdot SO_3H$	CCl_4	4—5	0·30±0·06
		20—24	0·78±0·05
		48	1·4±0·2
Ph·OH	C_6H_6	25	0·079±0·008
	CCl_4	4	0·16±0·01
		18	0·24±0·01
		54	0·31±0·01
	EtOH	20	0·17±0·05
	Et_2O	20	<0·03
	$COMe_2$	20	<0·03
o-Cresol	CCl_4	3	0·07±0·01
		19	0·10±0·01
		52	0·20±0·01
p-Cresol	CCl_4	3	0·13±0·01
		20	0·21±0·01
		53	0·27±0·01
Quinol ‡	EtOH	26	0·17±0·05
s-$C_6H_2Cl_3\cdot OH$	CCl_4	21	0·042±0·007
$C_6Cl_5\cdot OH$		17	0·078±0·006
o-$C_6H_4(OH)(NO_2)$		26	<0·001

* k_c extrapolated to zero conversion. † $C_4H_8O_2$ = dioxan.

‡ This catalyst is practically insoluble in carbon tetrachloride.

TABLE II.

Retardation of the acid-catalysed formation of cyclo*pentadiene–benzoquinone.*

(Solvent, carbon tetrachloride; initial concentration of reactants, 0·0200 g.-mol./l.)

Ref. no.	Retarder.	Catalyst.	Concn., in 10^{-3} g.-mol./l.		Temp.	k_c^r (l.^{2} g.-mol.$^{-2}$ min.$^{-1}$).	k_c^{II}/k_c^r.
			Re-tarder.	Cata-lyst.			
1	Pyridinium trichloroacetate	$CCl_3\cdot CO_2H$	1·0	4·5	15°	140	2·8
2	Diethylammonium trichloroacetate	$CCl_3\cdot CO_2H$	1·0	4·5	16	135	2·8
3	Triethylammonium trichloroacetate	$CCl_3\cdot CO_2H$	1·0	4·5	16	230	1·7
4	*sec.*-Butylammonium trichloroacetate	$CCl_3\cdot CO_2H$	1·0	4·5	18	222	1·7
5	(+)-Phenylethylammonium trichloroacetate	$CCl_3\cdot CO_2H$	1·0	4·5	18	255	1·5
6	Diethylammonium dichloroacetate	$CHCl_2\cdot CO_2H$	2·0	18·0	20	52	1·7
7	Pyridinium monochloroacetate	$CH_2Cl\cdot CO_2H$ *	1·0	32·0	18	6·6	2·0
8	*sec.*-Butylammonium acetate	$CH_3\cdot CO_2H$	100	480	15	0·14	3·6
9	Ethyl alcohol	$CCl_3\cdot CO_2H$	6·9	5·0	15	186	2·0
10	Nitromethane	$CCl_3\cdot CO_2H$	0·75	5·0	14	240	1·6
11	Acetonitrile	$CCl_3\cdot CO_2H$	0·75	5·0	12	225	1·7
12	Acetonitrile	$C_{10}H_7\cdot SO_3H$	0·8	10	15	56	1·4
13	Chloroform	$CCl_3\cdot CO_2H$	0·48	5·0	15	284	1·4
14	*o*-Dichlorobenzene	$CCl_3\cdot CO_2H$	3·5	5·0	14	106	3·9

* Attempts were made to retard this acid catalysis by pyridinium trichloroacetate; no retardation could be observed, however, probably owing to an exchange reaction involving the formation of free trichloroacetic acid.

was relatively low. At higher concentrations discrepancies were noted,* and if this was the case the c value was taken to be the mean of the concentration estimated with the help of the two methods. In the runs with hydrochloric acid the acid titre of the reaction mixture decreased relatively rapidly, owing to the addition of the acid to the double bonds of *cyclo*pentadiene; the k_c^{I} values had to be related, therefore, to the initial stage of this catalysis, and the hydrochloric acid concentration was calculated from the amount of acid added at the time of mixing.

It has been shown in Part I that the trichloroacetic acid catalysis of (1) in benzene solution is retarded on addition of the polar reaction product. We have now observed that other polar substances also retard or inhibit the catalysis by all the acids here considered. Velocity coefficients relating to a particular retarder concentration $[r]$ are designated by k_c^r and were computed from (5). In two sets of experiments the k_c^r values were determined for different retarder concentrations and it was found that the following equation holds

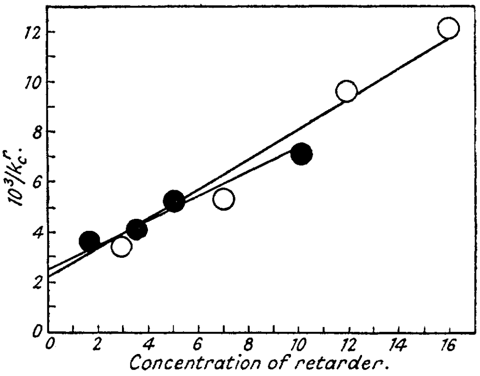
$$1/k_c^r = \alpha[r] + \beta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where α and β are parameters, the significance of which will be discussed below.

Catalysis of Reaction (1).—Typical data showing the effects brought about by trichloroacetic acid in carbon tetrachloride solution are represented by the graphs in Fig. 1. Similar experiments were carried out with other catalysts and solvents. In some of these tests k_c^{II} decreased with increasing conversion (cf. Part I), probably owing to a retardation by the polar *cyclo*pentadiene–benzoquinone. The initial k_c^{II} values were independent of the initial concentration of the reactants, and it is concluded, therefore, that these catalytic processes are of the second order in the substrate. Typical results showing that the reactions are of the first order with respect to the catalyst have already been reported in Part I; further tests with other catalysts and solvents confirm the earlier observations. A summary of all the results is in Table I.

FIG. 2.

Influence of pyridinium trichloroacetate and ethyl alcohol on the trichloroacetic acid catalysis of the addition of cyclo*pentadiene to benzoquinone in carbon tetrachloride solution at* 17°; *initial concentration of reactants,* 0·0200 *g.-mol./l.*



Black circles : Pyridinium trichloroacetate ; concentration scale is 10^{-4} *g.-mol./l.; concentration of trichloroacetic acid* = 0·00450 *g.-mol./l.*

Open circles : Ethyl alcohol ; concentration scale in 10^{-3} *g.-mol./l.; concentration of trichloroacetic acid* = 0·00450 *g.-mol./l.*

The influence of pyridinium trichloroacetate and ethyl alcohol (typical retarders) on the trichloroacetic acid catalysis is shown in Fig. 2.

Further rate measurements were made in which the initial concentration of the reactants and the concentration of the pyridinium salt were respectively 0·0200 and 0·00100 g.-mol./l., while the trichloroacetic acid concentration was varied between 0·045 and 0·009 g.-mol./l. There was no trend of the k_c^r values although the observations cover the range up to 70% conversion. Other substances which act as retarders are listed in Table II, the effects being shown by the figures in the last two columns.

Attempts were made to retard the phenol catalysis by the addition of pyridinium phenoxide or pyridinium trichloroacetate, but no effect could be observed.

The influence of hydrochloric acid in hexane, benzene, or carbon tetrachloride could not be tested because an insoluble addition product with benzoquinone is quickly formed, the precipitation of which prevents application of the colorimetric technique. In carefully purified ethyl alcohol at 4°, and at relatively high dilutions, the rate of this side reaction is slow, however, so that kinetic measurements are possible; under these conditions hydrochloric acid has no detectable catalytic effect. The following substances were also tested and found to be ineffective : the ethyl esters of trichloroacetic, dichloroacetic, and monochloroacetic acids; the methyl esters or ethers of acetic acid, phenol, and p-cresol; pyridine, pyridinium trichloroacetate, and trimethylamine. In these experiments the solvents were carbon tetrachloride or hexane, the temperature was between 0° and 26°, the initial concentration of the reactants was between 0·01 and 0·02 g.-mol./l., and the concentration of the added substance between 0·04 and 0·05 g.-mol./l.

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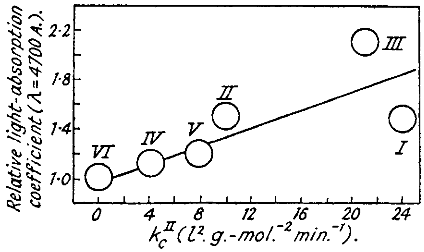
* These may be due to the occurrence of side reactions of the type described by Bruson (U.S.P. 2,395,452).

The relationship between the catalytic activity of phenols and the relative increase of the light absorption, due to the addition of these catalysts to solutions of benzoquinone, is shown in Fig. 3.

Catalysis of Reaction (2).—The dilatometer readings of a typical experiment with trichloroacetic acid are shown by graph *A* in Fig. 4; l_t is the reading at time t, and l_∞, the final reading, was obtained as indicated on p. 3047.

FIG. 3.

Relative light absorption of phenol–benzoquinone mixtures in carbon tetrachloride solution at 20°; *comparison with catalytic activity of the phenols.*

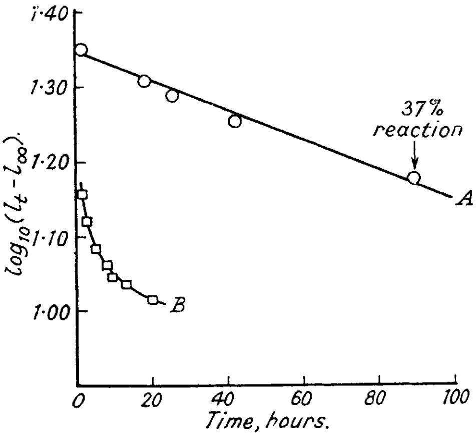


I, *Phenol.* II, o-*Cresol.* III, p-*Cresol.* IV, 2 : 4 : 6-*Trichlorophenol.* V, *Pentachlorophenol.* VI, o-*Nitrophenol. Concentrations of* I—VI, 0·114 *g.-mol./l.*; *in the test with* VI *the comparison absorption cell contained an* o-*nitrophenol solution of the same concentration. In all experiments the concentration of the reaction mixture with respect to benzoquinone was* 0·0200 *g.-mol./l. The absorption coefficients plotted on the ordinate are relative to a benzoquinone solution of this concentration, but without addition of a phenol.*

The slope of graph *A* corresponds to a catalytic velocity coefficient of 5·4 × 10^{-4} l. g.-mol.$^{-1}$ min.$^{-1}$; after taking into account the last term of (6) the corrected k_c^{I} value is 4·4 × 10^{-4} l. g.-mol.$^{-1}$ min.$^{-1}$. The results of some of the rate measurements with trichloroacetic acid and carbon tetrachloride as a solvent are in Fig. 5, similar tests having also been done at 20°, 0°, and −7°. A summary of the results relating also to other acids and solvents is in Table III. The figures in cols. 4 and 5 show in which concentration range the rate equations were tested and found to be valid.

FIG. 4.

Acid catalysis of the dimerisation of cyclo*pentadiene in carbon tetrachloride solution at* 25·0°; k = 4·1 × 10^{-5} *l.g.-mol.*$^{-1}$ *min.*$^{-1}$.



(*A*) *Trichloroacetic acid*; *initial concentrations of* C_5H_6 *and catalyst, respectively,* 1·55 *and* 0·160 *g.-mol./l.*; *mean value of catalyst concentration, taking titration results into account, is* 0·130 *g.-mol./l.*

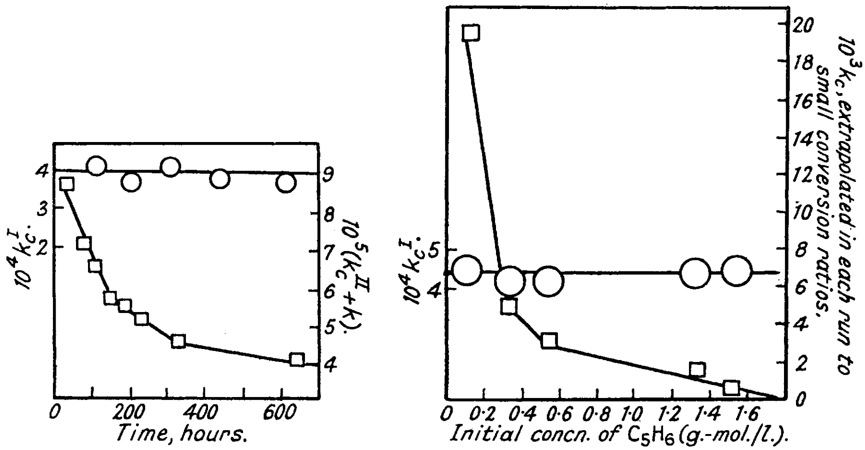
(*B*) *Hydrochloric acid*; *initial concentration of* C_5H_6 *and catalyst, respectively,* 0·310 *and* 0·0800 *g.-mol./l.*

In some experiments with trichloroacetic acid and carbon tetrachloride as solvent traces of moisture were removed from the reactants, catalyst, and solvent, and the reaction mixture was filled into the dilatometers without exposing it to atmospheric moisture. Furthermore, tests were done in which the surface/volume ratio of the dilatometer vessel was increased from 2 to 17 cm.$^{-1}$ and in which the reaction mixture was 0·002—0·05 M. with respect to benzoyl or di*cyclo*pentadiene peroxide. No change of rate could be detected in any of these experiments.

The k_c^{I} values in lines 11 and 12 of Table III, relating to hydrochloric acid, were calculated from the initial slope of such graphs as *B* in Fig. 4, the marked deviation from linearity being probably due to the reaction referred to on p. 3049. Hydrobromic acid was tested at −7° and it was found that the catalytic effect and the kinetics are similar to those of hydrochloric acid.

FIG. 5.

Trichloroacetic acid catalysis of the dimerisation of cyclo*pentadiene in carbon tetrachloride solution at* 25°.



Circles : left ordinate ; these graphs show that equation (6) *applies. Squares : right ordinate ; these graphs show that equation* (5) *does not apply.*

Left-hand figure : Results of a typical experiment ; a *and* c, *respectively,* 0·564 *and* 0·0200 *g.-mol.*/*l. The time scale covers the stage up to* 50% *conversion.*

Right-hand figure : Each circle is the result of measurements similar to those represented by the left-hand graph. Three of the circles are results of several tests in which the catalyst concentration was varied in the range 0·0100—0·160 *g.-mol.*/*l.*

TABLE III.

Acid catalysis in the dimerisation of cyclo*pentadiene.*

(10^5k in acetone and dioxan solution, at 25°, = 5·2 and 5·4 l./g.-mol.$^{-1}$ min.$^{-1}$. k_c^I in l. g.-mol.$^{-1}$ min.$^{-1}$; k_c^{II} in l.^{2} g.-mol.$^{-2}$ min.$^{-1}$.)

			Range of initial concn. (g.-mol./l.).		$k_c^I \times 10^3$, l. g.-mol.$^{-1}$ min.$^{-1}$ as derived from (6).	$k_c^{II} \times 10^3$, l. g.-mol.$^{-1}$ min.$^{-1}$ as derived from (5).
Catalyst.	Solvent.	Temp.	C_5H_6.	Catalyst.		
$CCl_3{\cdot}CO_2H$	CCl_4	25°	0·100—1·55	0·0100—0·160	0·40±0·05	
		20	0·310—1·55	0·0150—0·130	0·34±0·06	
		0	0·310—1·5	0·010 —0·270	0·16±0·04	
		−7	0·100—1·55	0·100	0·15±0·03	
	EtOH	25·0	0·565	0·0500		
	$COMe_2$	25·0	0·565	0·0500	<0·02	
	$C_4H_8O_2$	25·0	0·565	0·0500		
$CHCl_2{\cdot}CO_2H$	CCl_4	25·0	0·100—0·565	0·150—0·600	0·20 ±0·03	
$CH_2Cl{\cdot}CO_2H$		25·0	0·100—0·310	0·160	0·10 ±0·02	
$CH_3{\cdot}CO_2H$		25·0	0·310—1·55	1·00*	0·018±0·002	
HCl	CCl_4	25·0	0·084—1·55	0·0200 —0·0700	7±2	
		−7	0·310—1·55	0·00900—0·0900	3±1	
$C_{10}H_7{\cdot}SO_3H$	CCl_4	40	1·55	0·0300		7·6 ±0·8
		25	0·310—1·55	0·00600—0·0200		1·5 ±0·5
		0	0·565	0·0100 —0·0300		0·10±0·03
	EtOH	25	0·565	0·300		<0·1

* Tests with higher acetic acid concentrations were also done but under these conditions k_c^{II} decreases very markedly : it is possible that this due to a " solvent " effect similar to that operating in the runs with ethyl alcohol as solvent.

Poly*cyclo*pentadienes, dissolved in carbon tetrachloride, are precipitated on addition of acetone. Under the conditions of the experiments, the results of which are listed in Table III, no such precipitation occurred if acetone was added at the end of the test. It is concluded, therefore, that the relevant velocity coefficients relate to (2) and not to a simultaneous polymerisation reaction. This is confirmed by the results of the experiments given in Table IV.

Some of the k_c^I values listed in Table III were deduced from graphs plotted in the manner recommended by Guggenheim (*Phil. Mag.*, 1926, **7**, 538) ; they agreed within the limits of the experimental errors with velocity coefficients estimated from such graphs as *A* in Fig. 4. This could not be expected if under the conditions of these measurements a polymerisation occurred to any appreciable extent, because control tests showed that the $l_0 - l_\infty$ value relating to the formation of poly*cyclo*pentadiene is 80—100% larger than that relating to (2).

TABLE IV.

Stoicheiometric relationship in the trichloroacetic acid catalysis of the dimerisation of cyclo*pentadiene.*

Temp. 25°. Initial concn. of C_5H_6 and catalyst, respectively, 1·55 and 0·16 g.-mol./l.

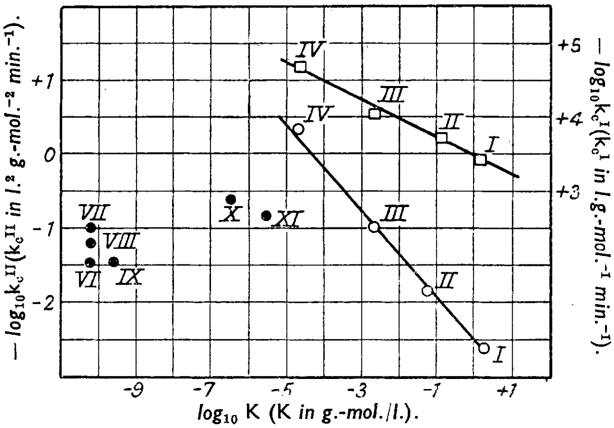
	Concn. of C_5H_6 (g.-mol./l.) calculated from :		Concn. of $C_{10}H_{12}$ (g.-mol./l.) calculated from :	
Time (hrs.).	dilatometer reading.	colorimetric determination of C_5H_6.*	dilatometer reading.	fractional distillation of reaction mixture.
28·5	1·04	1·12	—	—
120·3	0·52	0·43	0·51	0·47

* As described in *J.*, 1936, 1033.

The trichloroacetic acid catalysis in carbon tetrachloride solution (25°) can be completely inhibited if the reaction contains a relatively small amount of ethyl alcohol. In a typical experiment of this kind the concentrations (g.-mol./l.) of *cyclo*pentadiene, trichloroacetic acid, and ethyl alcohol were respectively 0·565, 0·0500, and 0·0500. Attempts were made to find out whether the rate of (2) is altered on addition of phenol, diethylamine, sodium acetate, or potassium hydroxide, these tests being done either in carbon tetrachloride or in ethyl alcohol solution. No effect could be detected.

FIG. 6.

Functional relation between acidity and catalytic activity.



Dots : phenol catalysis of reaction (1). *Circles : acid catalysis of reactiou* (1). *Squares : acid catalysis of reaction* (2). *Dots and circles : left ordinate. Squares : right ordinate.* I, *Trichloroacetic acid.* II, *Dichloroacetic acid.* III, *Monochloroacetic acid.* IV, *Acetic acid.* VI, *Phenol.* VII, o-*Cresol.* VIII, *Quinol.* IX, p-*Cresol.* X, *Trichlorophenol.* XI, *Pentachlorophenol.*

TABLE V.

Activation energies and non-exponential factors of the Arrhenius equation.

The *A* values of the bimolecular associations and the A_c values relating to the trichloroacetic acid and the hydrochloric acid catalysis of reaction (2) are in l. g.-mol.$^{-1}$ sec.$^{-1}$; all the other A_c values are in l.^{2} g.-mol.$^{-2}$ sec.$^{-1}$.

		$\log_{10} A_c$.		E_c (kcals.).		$\log_{10} A/A_c$.		E—E_c (kcals.).	
Catalyst.	Solvent.	Reaction (1).	Reaction (2).	Reaction (1).	Reaction (2).	Reaction (1).	Reaction (2).	Reaction (1).	Reaction (2)
$CCl_3·CO_2H$	C_6H_{12}	2·8±0·8 *		3·0±1·0 *		3·7±1·3		8·6±1·4	
	C_6H_6	0·6±0·8 †		0·0±1·0 †		5·9±1·6		12·1±1·5	
	CCl_4	0·8±0·6	−1·1±1·5	0·0±0·8	5±2	3·5±0·9	5·2±1·8	8·8±1·2	12±2
$CHCl_2·CO_2H$	CCl_4	1·0±0·6		3·4±0·8		3·3±0·9		5·4±1·2	
$CH_2Cl·CO_2H$		2·5±0·6		4·3±0·8		1·8±0·9		4·5±1·2	
$CH_3·CO_2H$		3·9±0·9		7·9±1·0		0·4±1·2		0·9±1·4	
$C_{10}H_7·SO_3H$		3·4±0·6	7·6±0·8	4·5±0·8	16±1	0·9±0·9	−0·9±1·1	4·3±1·2	1±1·4
HCl			−2±2		4±2·5		−8·7±2·3		13±3
Phenol		1·4±0·7		2·5±0·5		2·9±1·0		6·3±1·3	
o-Cresol		2·2±0·7		3·9±0·9		2·1±1·0		4·9±1·3	
p-Cresol		1·3±0·7		2·4±0·9		3·0±1·0		6·4±1·3	

* Calculated from velocity coefficient, extrapolated to zero conversion.

† Taken from Part I.

Some Numerical Relationships.—In Fig. 6 the logarithms of some of the catalytic velocity coefficients listed in Tables I and III are plotted against the logarithm of the dissociation constant, K, of the relevant catalyst, the latter values relating to water as solvent. The K value of trichloroacetic acid was calculated as suggested by Bell (*Proc. Roy. Soc.*, 1934, **143**, 389), the dissociation constants of the cresols were taken from Ward (*J.*, 1915, **107**, 1540), those of the chlorophenols from Thiessen (*Rec. Trav. chim.*, 1929, **48**, 1066), and those of the remaining catalysts from Landolt–Börnstein's Tables.

The catalysis of the carboxylic acids can be represented by

$$\log_{10} k_c = -m \log_{10} K + n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where m and n are respectively 0·57 and 2·6 in reaction (1) and 0·25 and 0 in the case of association (2), if the dimensions of k_c and K are as specified in the figure. No such relation is obtained, however, in the phenol catalysis.

The velocity coefficients of the non-catalysed and of the catalysed diene syntheses can be represented by

$$k = A\mathrm{e}^{-E/\boldsymbol{R}T} \text{ and } k_c = A_c\mathrm{e}^{-E_c/\boldsymbol{R}T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The A_c and E_c values relating to some of the catalysed processes are listed in Tabe V; for the sake of comparison the ratios A/A_c and the values for $E - E_c$ are also given, the figures for A and E being taken from previous work (*loc. cit.*). The graph in Fig. 7 shows a linear functional relationship between some of these A_c values and the corresponding activation energies.

DISCUSSION.

Acid Catalysis.—The kinetics are interpreted with reference to the following steps :

$$\mathrm{S + HB} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \overset{+}{\mathrm{HS}} \cdots\cdots \overset{-}{\mathrm{B}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$\left.\begin{aligned} &\overset{+}{\mathrm{HS}} \cdots\cdots \overset{-}{\mathrm{B}} + \mathrm{S} \xrightarrow{k_2} \overset{+}{\mathrm{HSS}} \cdots\cdots \overset{-}{\mathrm{B}} \\ &\overset{+}{\mathrm{HSS}} \cdots\cdots \overset{-}{\mathrm{B}} \xrightarrow{k_3} \mathrm{SS + HB} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$\overset{+}{\mathrm{HS}} \cdots\cdots \overset{-}{\mathrm{B}} + \mathrm{r} \xrightarrow{k_4} \mathrm{r} \cdots \mathrm{HB + S} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

or

$$\overset{+}{\mathrm{HS}} \cdots\cdots \overset{-}{\mathrm{B}} + \mathrm{r} \xrightarrow{k_4} \overset{+}{\mathrm{HS}} \cdots \overset{-}{\mathrm{B}} \cdots\cdots \mathrm{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where the substrate, S, is benzoquinone or *cyclo*pentadiene, HB is the acid, which may be wholly associated to form double molecules, SS is the product, r is one of the retarders listed in Table II, and the symbols $\mathrm{HS^+ \cdots B^-}$ or $\mathrm{HSS^+ \cdots B^-}$ indicate ion-pairs formed by protolytic fission of the acid. Assuming that the relative values of the velocity coefficients k_1, k_{-1}, etc., are such as to allow application of the stationary state approximation, it can be shown that the overall catalytic rate is given by

$$k_1k_2[\mathrm{S}]^2[\mathrm{HB}]/(k_{-1} + k_2[\mathrm{S}] + k_4[\mathrm{r}]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

[S] and [HB] having the same significance as a and c in equations (3) and (6). On taking the reverse process (12) into account a different expression is obtained which reduces to (14) if $k_1[\mathrm{HB}] \gg k_{-4}[\mathrm{r} \cdots\cdots \mathrm{HB}]$, where k_{-4} is the velocity coefficient of the reaction between the retarder–catalyst complex, r–HB, and the substrate.

In the absence of retarders the last term in the denominator of (14) can be omitted, and in this case the catalytic rate is either of the second or of the first order with respect to the substrate according to whether (15) or (16) holds, and the experimental velocity coefficients, k_c, as derived from (5) or (6) are given by (17) or (18) :

$$k_{-1} \gg k_2[\mathrm{S}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

$$k_2[\mathrm{S}] \gg k_{-1} \text{ and therefore } k_2 \gg k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$k_c^{\mathrm{II}} = k_1k_2/k_{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$k_c^{\mathrm{I}} = k_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

It is of interest to estimate the rate of (1) as catalysed by the carboxylic acids, on making the tentative assumption that the substrate reacting in step (10) is *cyclo*pentadiene. It follows from (15) that $k_2/k_{-1} \ll 1/[\mathrm{S}]$ and, substrate concentrations such as those listed in Table I being used, the upper limit of this ratio of velocity coefficients is 50 l. g.-mol.$^{-1}$. In accordance with the premise, the k_1 values of both diene associations are identical and can be taken to vary in the range $0{\cdot}2 \times 10^{-4}$ to 4×10^{-4} l. g.-mol.$^{-1}$ min.$^{-1}$, the solvent being that indicated in the first line of Table III and the temperature being 25°. On substitution of these k_1 values and the upper limit of k_2/k_{-1} in (17), it follows that the velocity coefficients, k_c^{II}, of reaction (1) should be at the most 0·02 l.^{2} g.-mol.$^{-2}$ min.$^{-1}$, while the actually determined velocity constants, as listed in lines 6, 14, and 19 of column 4, and line 3 of the last column of Table I, are between 25 and 20,000 times larger. It can be concluded, therefore, that the substrate of step (10) is benzoquinone rather than *cyclo*pentadiene, and that the velocity coefficients k_1, relating to the former reactant, are considerably larger than the k_c^{I} values in Table III.

It has already been mentioned (p. 3047) that the naphthalene-2-sulphonic acid catalysis of the association (2) is of the second order with respect to *cyclo*pentadiene, in contrast to the catalysis by all the other acids listed in Table III. This is compatible, however, with (15) and (16) if one assumes that $k_2^n/k^n_{-1} \ll k_2^b/k^b_{-1}$, the superscripts relating respectively to naphthalene-2-sulphonic acid and to the acids of group (*b*). It may be that $k^n_{-1} \gg k^b_{-1}$, or that $k_2^n \ll k_2^b$; there is no difficulty in accounting for the latter inequality because one component of the ion-pair reacting in step (11) is relatively bulky if naphthalene-2-sulphonic acid is the catalyst, and it is plausible to expect that this should give rise to a slow association reaction.

Brønsted (for reference see Bell, " Acid-Base Catalysis," Oxford, 1941) pointed out that relationships similar to (8) hold in many proton-transfer reactions and, in view of such equations as those presented by Bell (*op. cit.*, p. 168), the two graphs of Fig. 6 appear to support the suggested mechanism. It has to be taken into account, however, that the dissociation constants, K, in (8) relate to the protolytic equilibrium $H_2O + HB \rightleftharpoons H_3O^+ + B^-$, which is a reaction comparable to (10), while the catalytic velocity coefficients, k_c, are given by (17) or (18) rather than by k_1/k_{-1}. The actually observed validity of (8) implies, therefore, that in reaction (1) the velocity coefficients k_2 change less markedly than the ratio k_1/k_{-1} and that in the association (2) the k_{-1} values remain relatively constant.

The retarders Nos. 1—8 of Table II are salts, which probably act as ion-pairs, *viz.*, $R_1R_2R_3HN^+ \cdots B^-$; and Nos. 9—14 are also relatively polar substances, some of which contain oxygen or nitrogen, with lone electron-pairs, while others, *e.g.*, Nos. 13 and 14, cannot be regarded as proton acceptors in the recognised sense. It is believed that in all cases the retardation depends on the formation of a dipole association complex.* If this should involve a liberation of the substrate, as indicated by (12), it is feasible that the primary formation of the retarder–catalyst complex is followed by a proton transfer of the type $HB \cdots r \rightleftharpoons Hr^+ \cdots B^-$. If, on the other hand, the retarder forms a complex with the whole ion-pair [(see (13)], the decrease of the catalytic rate could be interpreted as a dipole screening by which the reactivity of the ion-pair $HS^+ \cdots B^-$ is reduced. It is recognised that (12) and (13) imply that a consumption of the catalyst by the retarder takes place. The figures in cols. 4 and 5 of Table II show, however, that the concentration of the retarder is in all cases considerably smaller than that of the catalyst, and it is understandable why the velocity coefficients k_c^r do not decrease to any detectable extent with increasing conversion of the reactants.

According to (14) retardation of the overall reaction is compatible either with $k_4[\mathrm{r}] \gg \{k_2[\mathrm{S}] + k_{-1}\}$ or with $k_4[\mathrm{r}] + k_{-1} \gg k_2[\mathrm{S}]$, the latter inequality leading to a dependence of $1/k_c^r$ on the retarder concentration, such as that represented by (7). The parameters α and β can be identified, therefore, with $k_4/k_c^{\mathrm{II}}k_{-1}$ and with $1/k_c^{\mathrm{II}}$, and taking into account the dimension and the numerical values of the slopes of the graph in Fig. 2, it follows that

$$\left.\begin{array}{l} k_4/k_{-1} = 1{\cdot}6 \times 10^3 \text{ l. g.-mol.}^{-1} \text{ (for pyridinium trichloroacetate)} \\ k_4/k_{-1} = 2{\cdot}4 \times 10^2 \text{ l. g.-mol.}^{-1} \text{ (for ethyl alcohol)} \end{array}\right\} \quad . \quad . \quad . \quad (20)$$

Phenol Catalysis.—It has been suggested by Woodward (*J. Amer. Chem. Soc.*, 1942, **64**, 3058) that uncatalysed diene associations involve intermediates formed by an electron transfer similar to that discussed by Weiss (*J.*, 1942, 245). This mechanism cannot be reconciled with the observed similarity of the kinetics of bimolecular Diels–Alder reactions in the gaseous and condensed phase (Wassermann, *Trans. Faraday Soc.*, 1938, **34**, 128; *J.*, 1939, 870) and with the results of unpublished experiments done in order to detect a relation between the rate of these associations and the occurrence of transient colours which are obtained in some systems on mixing the reactants. Woodward's hypothesis is of importance, however, for an interpretation of the phenol catalysis of reaction (1). The kinetics can be explained with reference to the following steps :

$$\mathrm{S} + \mathrm{HB} \underset{k_{-\mathrm{I}}}{\overset{k_{\mathrm{I}}}{\rightleftharpoons}} \bar{\mathrm{S}} \cdots\cdots \mathrm{H} \cdots\cdots \overset{+}{\mathrm{B}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$\left.\begin{array}{lcl} \bar{\mathrm{S}} \cdots \mathrm{H} \cdots \overset{+}{\mathrm{B}} + \mathrm{S} & \xrightarrow{k_{\mathrm{II}}} & \mathrm{S}\bar{\mathrm{S}} \cdots \mathrm{H} \cdots \overset{+}{\mathrm{B}} \\ \mathrm{S}\bar{\mathrm{S}} \cdots \mathrm{H} \cdots \overset{+}{\mathrm{B}} & \xrightarrow{k_{\mathrm{III}}} & \mathrm{SS} + \mathrm{HB} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

---

* If the influence of acids on the rate of these diene associations were due to a reaction involving hydrogen ions rather than the whole acid molecules one would have to consider whether the retardation by the salts Nos. 1—8 in Table II is due to a repression of the acid dissociation of the catalysts (common-ion effect). However, in this case the catalytic rate should have been found to be proportional to the square root of the catalyst concentration and not to its first power.

Here $S^- \cdots H \cdots B^+$ indicates relatively deeply coloured ion-pairs, which can also be represented as hydrogen bonded species (cf. Weiss, *loc. cit.*) and are formed by an electron transition from a phenol, HB, to the benzoquinone, S, the other symbols having a similar significance to that in (10) and (11). It could be suggested that the electron acceptor is the *cyclo*pentadiene, not the benzoquinone; this is improbable, however, because it has been shown (p. 3052) that phenol does not catalyse the dimerisation (2). It appears that benzoquinone functions both as a proton and an electron acceptor, which is somewhat reminiscent of the amphoteric properties of certain polycyclic hydrocarbons (cf. Weiss, *loc. cit.*). Applying the stationary state approximation to (21) and (22), one can derive an expression similar to (14) without the last term of the denominator. The kinetics of the phenol catalysis are represented by (5), rather than by (6); this is to be expected, because the electron transfer (21) will be fast, making the overall reaction of the second order in the substrate, the catalytic velocity being given by

$$k_c^{\mathrm{II}} = k_{\mathrm{I}}k_{\mathrm{II}}/k_{-\mathrm{I}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

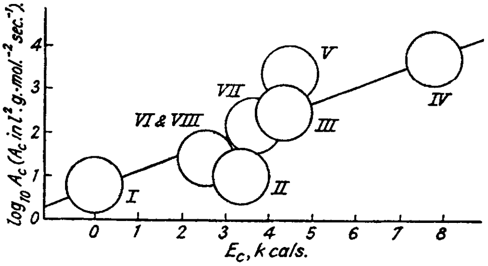
Pyridinium salts are effective retarders for acid catalysts, but in the phenol catalysis no such effect could be observed. This is what one would expect from the suggested electron-transfer mechanism because

$$k_{-\mathrm{I}} \gg k_{\mathrm{IV}}[\mathrm{r}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where k_{IV} is the velocity coefficient relating to a step similar to (12) or (13).

FIG. 7.

Functional linear relationship between activation energy, E_c, *and* $\log_{10} A_c$ *of diene association* (1); *the solvent is carbon tetrachloride.*



I, *Trichloroacetic acid.* II, *Dichloroacetic acid.* III, *Monochloroacetic acid.*
IV, *Acetic acid.* V, *Naphthalene-2-sulphonic acid.* VI, *Phenol.*
VII, o-*Cresol.* VIII, p-*Cresol.*

The phenols listed in Table I can be divided into three groups: (A) Phenol, *p*-cresol, *o*-cresol, and quinol, which are the most active catalysts; (B) tri- and penta-chlorophenol, which are less efficient; (C) *o*-nitrophenol which does not catalyse. On addition of the phenols of groups (A) and (B) to a benzoquinone solution a marked deepening of colour takes place, but no effect of this kind can be observed with *o*-nitrophenol; the relative extinction coefficients, by which the colour of these solutions is characterised, are given in Fig. 3, which also shows that, at comparable concentrations, phenol and the cresols give rise to deeper colours than the catalysts of group (B). This can be taken to indicate that in the case of the phenols (A) the ratio $k_{\mathrm{I}}/k_{-\mathrm{I}}$ is relatively large, *i.e.*, the formation of a coloured substrate–catalyst complex is favoured. If it is assumed that k_{II} depends less markedly on structural alterations than $k_{\mathrm{I}}/k_{-\mathrm{I}}$ it is understandable, in view of (23), why the k_c^{II} values of the phenols (A) are also relatively large.* The results of experiments represented by the dots on the left of Fig. 6 show that the phenols of group (B) are more acidic in water than those of group (A), while *o*-nitrophenol is a still stronger acid. The decrease of the catalytic activity of these phenols with increasing acid strength—which is in marked contrast to the validity of (8) in the case of the acid catalysis—is in accordance with the suggested electron-transfer mechanism, since chemical conditions which enhance the release of electrons from the catalyst, thereby increasing $k_{\mathrm{I}}/k_{-\mathrm{I}}$, will impede the release of protons.

---

* In some cases variations of k_{II} may contribute to the overall effects. Fig. 3 shows that the k_c^{II} values of phenol and *p*-cresol are similar, although the latter catalyst gives rise to a more intense colour on addition to a benzoquinone solution. It has also been observed that phenol and chloroanil form a relatively deeply coloured complex in benzene solution; the reaction between chloranil and *cyclo*pentadiene (see Part I) is nevertheless not catalysed by phenol.

Activation Energies and Kinetic A_c *Factors.*—The parameters of (9) listed in Table V can be divided into two groups relating respectively to the velocity coefficients k_c^{II} given by (17) and (23) and to the rate constants k_c^{I} given by (18). The A_c and E_c values of the first group are in cols. 3—5 and in line 7 of cols. 4 and 6, and can be represented by

$$A_c = A_1A_2/A_{-1} = BA_2, \text{ and by } E_c = E_{-1} - E_1 - E_2 \sim \Delta H - E_2$$

where the subscripts refer to the relevant subscripts of the k values in (17) and (23); B is a measure of the statistical weight of the associated species formed in (10) and (21), and ΔH is the heat change of these equilibria. One possible interpretation of the graph in Fig. 7 is based on the assumption that the parameters A_2 and E_2, relating to the specified catalysts and solvents, change less markedly than B and ΔH, so that the dependence of log A_c on E_c is essentially due to a similar dependence of log B on ΔH, which can be explained with reference to recognised correlations between entropies and energy changes (cf. Evans and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1333).

The A_c values of the second group in lines 3 and 8, col. 4, of Table V characterise the kinetics of step (11) of reaction (2) and here

$$A_c/Z \approx 10^{-12} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

where Z is the bimolecular collision frequency. It will be seen that the discrepancy between A_c and Z is very large. This may be due to the fact that the ion-pairs in (10) are formed *via* ionic transition states, which are more strongly solvated than catalyst and substrate taken separately. The increased solvation must give rise to an unfavourable entropy of activation, which accounts for the smallness of the A_c factors. The activation energy of these proton transfer processes is about 5 kcals. with an inaccuracy shown by the figures in lines 3 and 8, col. 6, of Table V. When (16) is taken into account it appears probable that the activation energy of the consecutive step $C_5H_7^+ \cdots B^- + C_5H_6 = C_{10}H_{13}^+ \cdots B^-$ is still smaller. The E value of the dimerisation $2C_5H_6 = C_{10}H_{12}$, on the other hand, is 17·4 kcals. (*J.*, 1939, *loc. cit.*), the difference being probably due to the fact that in the former association the *cyclo*pentadiene is strongly polarised in the field of the ion-pair, thereby facilitating the juxtaposition favourable for reaction. Geometrical considerations similar to those discussed elsewhere (*J.*, 1935, 828, 1511; *J.*, 1936, 432) show that these reactants must approach each other in a mutual orientation which is incompatible with the formation of "planar" transition states in which resonance energy can play a very important rôle.

Solvent Effects.—The data in Table I show that the rate of the trichloroacetic acid catalysis is of the same order in hexane, benzene, and carbon tetrachloride solutions. Strong retardation is observed, on the other hand, if the following solvents, of widely different dielectric constant (ε), are used: chloroform ($\varepsilon = 5{\cdot}0$), ether ($\varepsilon = 4{\cdot}5$), dioxan ($\varepsilon = 3{\cdot}0$), acetone ($\varepsilon = 21{\cdot}9$), and ethyl alcohol ($\varepsilon = 25{\cdot}7$). Similar effects were observed in the trichloroacetic and naphthalene-2-sulphonic acid catalysis of (2). The rate of the acetic acid catalysis of reaction (1), on the other hand, is larger in ethyl alcohol than in carbon tetrachloride solution. The catalytic velocity coefficients relating to phenol in benzene, carbon tetrachloride, and ethyl alcohol solutions are similar, but ether and acetone inhibit this catalysis. These results show that the k_c values may either increase or decrease with increasing dielectric constant of the solvent. This is understandable if one considers that steps (10) and (21) involve a charge separation which will be energetically facilitated by solvents of high ε values; in (11) and (22), on the other hand, the close proximity between the uncharged substrate and the ion-pair will be favoured by media of low dielectric constant. It can be concluded, therefore, that the ratios k_1/k_{-1} and $k_{\mathrm{I}}/k_{-\mathrm{I}}$ will increase while the velocity coefficients k_2 and k_{II} will decrease with increasing ε, an *a priori* estimation of the relative magnitude of these opposing effects being hardly feasible. It has to be taken into account, moreover, that ethyl alcohol and chloroform are retarders of the trichloroacetic acid catalysis (see Nos. 9 and 13 of Table II and p. 3052); it is probable, therefore, that some of the observed effects are due to steps (12) or (13) becoming predominant.

The Possibility of Partial Proton Transfer in the Acid Catalysis.—It could be suggested that steps (10)—(13) should be abandoned in favour of

$$\mathrm{S} + \mathrm{HB} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \mathrm{S} \cdots\cdots \overset{+}{\mathrm{H}} \cdots\cdots \overset{-}{\mathrm{B}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\left.\begin{array}{lcl} \mathrm{S} \cdots \overset{+}{\mathrm{H}} \cdots \overset{-}{\mathrm{B}} + \mathrm{S} & \xrightarrow{k_b} & \mathrm{SS} \cdots \overset{+}{\mathrm{H}} \cdots\cdots \overset{-}{\mathrm{B}} \\ \mathrm{SS} \cdots \overset{+}{\mathrm{H}} \cdots \overset{-}{\mathrm{B}} & \xrightarrow{k_c} & \mathrm{SS} + \mathrm{HB} \\ \mathrm{S} \cdots \overset{+}{\mathrm{H}} \cdots \overset{-}{\mathrm{B}} + \mathrm{r} & \xrightarrow{k_d} & \mathrm{r} \cdots \mathrm{HB} + \mathrm{S} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Here $S \cdots H^+ \cdots B^-$ and $SS \cdots H^+ \cdots B^-$ are symbols for hydrogen-bonded species formed by a partial proton transfer without complete disruption of a homopolar bond of the catalyst. Such intermediates are similar in certain respects to those formed in (21) and (22), both types being comparable to molecular compounds which are rapidly formed from their components (for reference, see Weiss, *loc. cit.*). Applying the stationary-state approximation to (26) and (27), we obtain an expression for the over-all rate which can be made to obey the experimental rate law (6) if one postulates that $k_b[S] \gg k_{-a}$ or $k_b \gg k_a$. If, therefore, the first-order dependence on the substrate concentration is to be explained, one has to make the improbable assumption that a step leading to a relatively loose complex is slower than one in which main valency bonds are broken and formed. On the basis of a partial proton-transfer mechanism one would expect furthermore an inequality similar to (24), which would not be compatible with the various results represented by the figures in Table II and with (20). Finally, it should be noted that (26) could not occur *via* a completely ionised transition state, so that it is not easy to account for the exceptionally small ratio (25).

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