127. *Homogeneous Catalysis of Diene Syntheses. A New Type of Third-order Reaction.*

By Albert Wassermann.

The rate of diene syntheses (Diels–Alder reactions) is not detectably altered on addition of iodoacetic acid, *p*-toluenesulphonic acid, pyridine, 2 : 2′-dipyridyl, three salts of heavy metals, iodine, *trans*-stilbene, oxygen, peroxides, acetonitrile, or ethyl trichloroacetate. Trichloroacetic acid, on the other hand, as well as a number of other acids, one base (*viz.*, trimethylamine), and α-naphthaquinone, are catalytically active. The latter tests were made in both polar and non-polar solvents, and in one association a rate-accelerating effect of an acid could also be detected in the gas phase, there being no doubt that all the catalytic processes are homogeneous. An investigation of the kinetics of a selected set of catalytic processes showed that the primary step is of the third order and that the activation energy is near to zero.

Experiments are described relating to the catalysis of the following associations which are all typical diene syntheses :

*cyclo*Pentadiene + Benzoquinone = *cyclo*Pentadiene–benzoquinone . . . . (I)
*cyclo*Pentadiene + α-Naphthaquinone = *cyclo*Pentadiene–α-naphthaquinone . . . . . . (II)
2 *cyclo*Pentadiene = *endo*-Di*cyclo*pentadiene . . . . (III)
*cyclo*Pentadiene + *cyclo*Pentadiene–benzoquinone = Di*cyclo*pentadiene–benzoquinone . . . . (IV)
*cyclo*Pentadiene + Tetrachlorobenzoquinone = *cyclo*Pentadiene–tetrachlorobenzoquinone . . . . (V)

Catalytic tests involving 36 added substances were made; the results of the various sets of measurements, numbered for further reference, are in Table I.

Table I.

Influence of various added substances on the rate of diene syntheses.

Ref. No.	1.	2.	3.	4.	5.
Substance tested	H_2SO_4	H_3PO_4	HCl	12 Organic bases	$CH_2I{\cdot}CO_2H$
Solvent	Paraffin	Paraffin	EtOH	EtOH and C_6H_6	C_6H_6
Diene synthesis	III	III	I	I	I
Catalytic efficiency	?	?	?	?	—
Ref. No.	6.	7.	8.	9.	10.
Substance tested	*p*-$C_6H_4Me{\cdot}SO_3H$	C_5H_5N	2 : 2′-Dipyridyl	$FeCl_3$	$CuCl_2$
Solvent	EtOH	C_6H_6	C_6H_6	EtOH	EtOH
Diene synthesis	I	I	I	I	I
Catalytic efficiency	—	—	—	—	—
Ref. No.	11.	12.	13.	14.	15.
Substance tested	$MnCl_2$	I_2	*trans*Stilbene	O_2	Di*cyclo*pentadiene peroxide
Measurements done in	EtOH	C_6H_6	EtOH	C_6H_6, CCl_4, gas	$C_{10}H_{12}$
Diene synthesis	I	I	I	I and III	III
Catalytic efficiency	—	—	—	—	—
Ref. No.	16.	17.	18.	19.	20.
Substance tested	Bz_2O_2	MeCN	$CCl_3{\cdot}CO_2Et$	PhOH	$CH_2Br{\cdot}CO_2H$
Solvent	C_5H_6	CCl_4	C_6H_{14}	C_6H_6	C_6H_6
Diene synthesis	III	III	I	I	I
Catalytic efficiency	—	—	—	+	+
Ref. No.	21.	22.	23.	24.	25.
Substance tested	$CH_2Cl{\cdot}CO_2H$		$CCl_3{\cdot}CO_2H$		NMe_3
Solvent	C_6H_6	EtOH	C_6H_{14}	C_6H_6	C_6H_6
Diene synthesis	I	I	I	I	I
Catalytic efficiency	+	+	+	+	+
Ref. No.	26.	27.	28.	29.	30.
Substance tested	$CCl_3{\cdot}CO_2H$	α-Naphthaquinone	$CCl_3{\cdot}CO_2H$	NMe_3	$CH_3{\cdot}CO_2H$
Measurements done in	C_6H_6	C_6H_6	C_6H_6 and Paraffin	C_6H_6	Gas
Diene synthesis	II	I	III, IV, V	V	III
Catalytic efficiency	+	+	+	+	+

The experiments with sulphuric, phosphoric and hydrochloric acids and certain organic bases did not lead to conclusive results. Iodoacetic acid,* *p*-toluenesulphonic acid,* pyridine,* 2 : 2′-dipyridyl,* three salts of heavy metals,* iodine,* *trans*-stilbene,* oxygen,* peroxides,* acetonitrile,* and ethyl trichloroacetate are ineffective, but phenol, bromoacetic acid,† chloroacetic acid, trichloroacetic acid, trimethylamine, α-naphthaquinone, and acetic acid are catalytically active. These experiments were carried out in polar and non-polar solvents and in one case a rate-accelerating effect was found to occur in the gas phase, all the catalysed diene syntheses being entirely homogeneous.

---

* The experiments involving the substances indicated by an asterisk have already been described in previous papers; for references, see this vol., p. 623 (cf. also J., 1935, 828).

† This acid was described as being inactive (see J., 1935, 828); more accurate measurements showed, however, that there is a weak catalytic effect.

In attempting to elucidate the kinetics of the catalysed reactions Nos. 19—26, velocity coefficients, v_c, were calculated from

$$dx/dt = v_c(a - x)^2 c + v(a - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a and $a - x$ are the equimolar concentrations of the reactants at zero time and time t, respectively, c is the stoicheiometric concentration of the rate-accelerating added substance, and v is the bimolecular velocity coefficient of the non-catalysed diene syntheses taken from earlier papers of this series (J., 1935, 828; 1936, 1028). The various v_c values are in Table II, which also refers to the temperature and concentration range in which (1) was tested and to the number of runs in each set of measurements.

TABLE II.

Catalytic velocity coefficients, v_c, *relating to the formation of* cyclo*pentadiene–benzoquinone and* cyclo*pentadiene–α-naphthaquinone.*

Ref. No.	Diene synthesis.	Catalyst.	Solvent.	Temp.	$\log_{10} v_c$.*	Concentration range (g.-mols./l.). Catalyst.	Concentration range (g.-mols./l.). Reactant at $t = 0$.	No. of runs.
19	I	PhOH	C_6H_6	25°	-0.9 ± 0.1	0·0012—0·2	0·02	6
20		$CH_2Br\cdot CO_2H$		25	-0.70 ± 0.06	0·01—0·04	0·02	2
21		$CH_2Cl\cdot CO_2H$		25	-0.70 ± 0.06	0·0025—0·04	0·02	3
22		$CCl_3\cdot CO_2H$	EtOH	21	-0.22 ± 0.07	0·01	0·005	1
23			C_6H_{14}	25	$+0.58 \pm 0.04$	0·0025—0·01	0·02	4
24			C_6H_6	12·5	$+0.52 \pm 0.04$	0·005	0·02	1
				20	$+0.51 \pm 0.04$	0·005	0·02	1
				25	$+0.48 \pm 0.04$	0·0025—0·01	0·005—0·03	10
				39	$+0.52 \pm 0.04$	0·005	0·02	1
				53	$+0.36 \pm 0.12$	0·005	0·02	1
25		NMe_3		12	-0.1 ± 0.1	0·005—0·01	0·02	2
26	II	$CCl_3\cdot CO_2H$		25	$+0.04 \pm 0.04$	0·0025—0·01	0·02	5

* v_c is given in the units l.^{2} g.-mol.$^{-2}$ sec.$^{-1}$ both here and in Tables III and IV.

In Expts. Nos. 19—22 equation (1) was found to hold, the relevant catalytic velocity coefficients being the arithmetic means of the consistent v_c values as observed at various times and with different catalyst concentrations. In Expts. Nos. 23—26, on the other hand, the v_c values as deduced from (1) decrease with increasing time, probably owing to consecutive and reverse processes taking place * and to the formation of a relatively inactive complex between catalyst and product. The occurrence of the latter effect is indicated by experiments showing that *cyclo*pentadiene–benzoquinone acts as an inhibitor in the trichloroacetic acid catalysis of diene synthesis (I). The catalytic velocity coefficients Nos. 23—26 in Table II were estimated by plotting the relevant observed v_c values against time and extrapolating the graph so obtained to zero conversion. In all cases the initial v_c values were independent of the catalyst concentration, and in those runs in which tests were made there was also no detectable influence of the initial concentration of the reactants.

Atomic recombinations or acid- and base-catalysed reactions which have been the subject of previous kinetic investigations (cf. Bell, " Acid–Base Catalysis," Oxford, 1941, p. 114) do not take place at all in the absence of the catalyst, whereas the diene syntheses here considered proceed with measurable speed even in aprotic solvents or wholly in the gas phase, the non-catalysed associations being bimolecular. In the presence of the substances listed in col. 3 of Table II, a third-order catalysed reaction proceeds simultaneously with the bimolecular diene syntheses. This follows from the results of the kinetic measurements, which show that at least during the initial stage equation (1) is obeyed. A kinetic investigation of the catalytic processes Nos. 27—30 in Table I has not yet been carried out; it is believed, however, that the primary step is similar to that obtaining in Nos. 22—26.

It should be noted that the initial v_c value relating to the trichloroacetic acid catalysis of reaction (I) in benzene solution is not measurably affected by a temperature change within a range of about 40°; it follows, therefore, that the activation energy is numerically smaller than 1·5 kg.-cals.† This is an independent confirmation of the assumption that the reaction is of the third order, for it is known that some authentic third-order processes (*e.g.*, the reaction of nitrogen oxide with oxygen) are also characterised by relatively small activation energies.

It is intended to continue this research with a view to find out whether the homogeneous catalysis of diene syntheses is dependent on proton-transfer processes or whether an essentially different mechanism is operative.

EXPERIMENTAL.

The participants of reactions (I)—(IV) and the various solvents were purified by methods indicated in preceding parts of this series; the paraffin was the same specimen as that mentioned in J., 1939, 369; tetrachlorobenzoquinone and the product of reaction (V) were recrystallised respectively from benzene and ethyl alcohol, and all the substances which were tested for catalytic activity were recrystallised or redistilled and carefully dried. In the experiments with acids in ethyl-alcoholic solutions, titration tests showed that no detectable esterification had taken place. The stoi-

---

* In the case of diene synthesis (I), for instance, the consecutive process consists in the formation of di*cyclo*pentadiene–benzoquinone; the detectable influence of the reverse reaction is due to the fact that some of the runs were done at relatively high temperature.

† The overall activation energy relating to both the non-catalysed and the catalysed association amounts to about 3 kg.-cals. (cf. this vol., p. 624).

cheiometric equation of the catalysed addition of *cyclo*pentadiene to α-naphthaquinone, *cyclo*pentadiene–benzoquinone, and tetrachlorobenzoquinone was established by evaporating the solvent at the end of the reaction and weighing the purified residues, which were found to be identical with the products of the non-catalysed diene syntheses (II), (IV), and (V) and were obtained in a yield of at least 90% of the theoretical. In determining the stoicheiometric equation of the catalysed addition of *cyclo*pentadiene to benzoquinone, the product was first converted into di*cyclo*pentadiene–benzoquinone, the yield of which was then estimated as described above. This procedure had to be adopted because control experiments showed that in the presence of some of the catalysts *cyclo*pentadiene–benzoquinone is either decomposed during the evaporation of the solvent or undergoes subsequent changes leading to products which could not be identified. A typical experiment is as follows. 450 C.c. of a benzene solution, which at zero time was 0·09M with respect to *cyclo*pentadiene and benzoquinone and 0·05M with respect to trichloroacetic acid, are kept at 25° until 95% of the benzoquinone has reacted. Evaporation of the solvent at room temperature would now afford a non-crystallisable syrup, but if, instead, 6 c.c. of pure liquid *cyclo*pentadiene are added to the solution which is then kept at 50° for 54 hours, di*cyclo*pentadiene–benzoquinone can be isolated in a yield of 92% of the theoretical.

In order to establish that all the catalytic reactions referred to in this paper are homogeneous, control experiments with added glass powder or glass rods were carried out.

Reactions (I), (II), and (IV).—Velocity measurements were carried out by the methods already described (*locc. cit.*), all colorimetric determinations referring as before to filter S_{47} of the Zeiss Stufenphotometer. Hydrochloric acid in ethyl alcohol reacts with benzoquinone (cf. Gattermann–Wieland, "Die Praxis des Organischen Chemikers," Berlin, 1925, p. 281), thereby causing fading of its colour, the rate of fading being influenced by traces of impurities. It was not possible, therefore, to find out whether hydrochloric acid in ethyl alcohol is a catalyst for reaction (I) or not.

Attempts were made to follow the course of reaction (I) in the presence of methylamine, ethylenediamine, aniline, piperidine, 7-methylindole, pyrrole, cystein hydrochloride, glycylglycine, *l*-aspartic acid, *l*-leucine, *l*-tyrosine, and tryptophan. Deep colorations are produced on addition of a solution of benzoquinone in benzene or ethyl alcohol to any of the first seven bases; the other bases are also unsuitable for tests in ethyl alcohol or benzene, for their solubility is too small.

Control experiments showed that the extinction coefficient of benzoquinone is not measurably altered on addition of the substances listed in Nos. 18—25 and No. 27 of Table I, and that the colour of α-naphthaquinone is not detectably altered on addition of trichloroacetic acid.

TABLE III.

Catalysis of diene syntheses (I) and (II)—typical experiments.

Temp. : (22), (27) = 20°; (19), (20), (21), (23), (26) = 25°; (24), (25) = 12·5°.

Concn. of catalyst (g.-mols./l.) : (19) = 0·200; (20), (22), (26) = 0·0100; (21) = 0·00250; (23), (24), (25) = 0·00500; (27) = 0·00100.

Initial concn. of reactants (g.-mols./l.) : (22) = 0·00500; (19), (20), (21), (23), (24), (25), (26) = 0·0200; (27) = 0·001 ($C_6H_4O_2$) and 0·002 (C_5H_6).

Ref. No. (19).			Ref. No. (20).			Ref. No. (21).			Ref. No. (22).			Ref. No. (23).		
Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.	Time, mins.	η, cm.$^{-1}$.*	v_c.
10	0·246	6·8	20	0·268	12	20	0·278	12	5	0·0645	40	10	0·210	240
15	0·222	6·2	30	0·233	11	30	0·252	12	15	0·0585	30	20	0·176	220
22	0·154	5·8	40	0·223	11	40	0·232	12	30	0·0516	30	30	0·153	220
35	0·150	6·3	50	0·205	10	50	0·214	16	45	0·0456	40	40	0·138	200
59	0·104	5·4	60	0·188	12	60	0·200	12	—	—	—	50	0·127	188
												60	0·115	188

Ref. No. (24).			Ref. No. (25).			Ref. No. (26).			Ref. No. (27).		
15·5	0·245	206	16	0·297	46	35	0·131	57	400	0·0205	280
28·5	0·205	186	36	0·262	40	45	0·122	53	1556	0·0136	270
39·5	0·185	168	68	0·234	22	65	0·105	49			
63	0·149	158	109	0·198	22	108	0·0846	46			
101	0·122	132	234	0·150	10	168	0·0641	40			
162	0·0911	125									

* η = Extinction coefficient.

The effects of the various catalysts recorded in Nos. 19—27 of Tables I and II are shown by the data in Table III. Expt. No. 18 in Table I was done at 25°, the equimoarl initial concentration of the reactants being 0·02 g.-mol./l. The initial catalytic velocity coefficients relating to Nos. 23, 24, and 26 are listed in Table IV.

TABLE IV.

Initial catalytic velocity coefficients of trichloroacetic acid relating to the formation of cyclo*pentadiene–benzoquinone and* cyclo*pentadiene–α-naphthaquinone.*

	Concn., g.-mols./l. × 10^4.				Concn., g.-mols./l. × 10^4.				Concn., g.-mols./l. × 10^4.		
Temp.	Reactants at t = 0.	$CCl_3·CO_2H$.	v_c.	Temp.	Reactants at t = 0.	$CCl_3·CO_2H$.	v_c.	Temp.	Reactants at t = 0.	$CCl_3·CO_2H$.	v_c.
	Ref. No. (23).				Ref. No. (24).				Ref. No. (24), contd.		
25·0°	200	25	3·8	25·0°	200	25	2·7	25·0°	200	50	1·9 *
,,	200	50	4·0	,,	200	50	3·0	12·5	200	50	3·1
,,	200	100	3·7	,,	200	100	2·8	20·0	50	100	3·3
	Ref. No. (26).			,,	50	100	3·0	39·0	200	50	3·4
25·0°	200	25	1·0	,,	100	100	3·0	53·0	200	50	2·5
,,	200	50	1·1	,,	300	100	2·8				
,,	200	100	1·1								

* This velocity coefficient relates to a run in which the reaction mixture was at zero time 0·0117M with respect to *cyclo*pentadiene–benzoquinone. The decrease of the v_c values with increasing time is similar to that obtaining in experiment No. 24 of Table III.

The trichloroacetic acid catalysis of synthesis (IV) was investigated at 25° and in a solution 0·0433M with respect to the catalyst, the equimolar initial concentration of the reactants being 0·223 g.-mol./l. After 1300 mins., 79% of the *cyclo*pentadiene had been used; without catalyst, 30% of reaction had taken place under the same experimental conditions.

Reaction (*III*).—A mixture of *cyclo*pentadiene and trichloroacetic acid was dissolved in benzene or paraffin and kept for several days at temperatures between 0° and 25°; the reaction product was found to be not only di*cyclo*pentadiene but also a polymer or a mixture of polymers. Experiments with a view to study both the rate of the association and of the simultaneous or consecutive processes have not been done, since it is easier to investigate the trichloroacetic acid catalysis of the decomposition of di*cyclo*pentadiene. The equilibrium constant of reaction (III) cannot be substantially altered by addition of a relatively small amount of catalyst, and it follows that a substance catalysing the decomposition of di*cyclo*pentadiene will also catalyse the reverse association process. In studying the decomposition reaction in paraffin solution, the "second method" described in J., 1939, 379 was used. A number of control runs showed that diffusion processes are not rate-determining, and that trichloroacetic acid in paraffin solution does not give rise to evolution of a measurable amount of gas. The reaction vessel of 200 c.c. capacity contained in each run 25 c.c. of the solution, which was usually stirred at a speed of 750 r.p.m.; the burette in which the volumetric *cyclo*pentadiene determinations were carried out was kept at 52°. In a typical experiment the initial concentration of di*cyclo*pentadiene was 2·00 g.-mols./l., that of trichloroacetic acid was 0·0145 g.-mol./l., the pressure was 764 mm. of mercury, and the temperature of the reaction mixture was 135°. The volume of the gaseous *cyclo*pentadiene as obtained under these conditions is given in line 2 of Table V, and the data in line 3 refer to a control experiment without trichloroacetic acid. Similar experiments were carried out at 125°, 145°, and 155°, the concentration of the trichloroacetic acid being varied at each temperature from 0·008 to 0·03 g.-mol./l.

TABLE V.

Catalysis of the decomposition of di*cyclo*pentadiene *by trichloroacetic acid—typical experiment.*

Time, mins		4	8	12	16	20	25	30
Gaseous *cyclo*pentadiene, c.c.	With catalyst	3·5	6·2	7·8	9·0	10·0	10·4	11·4
	Without catalyst	1·5	2·5	3·2	3·5	3·8	4·4	4·5

A number of experiments were done on the decomposition of di*cyclo*pentadiene in paraffin solution in the presence of syrupy phosphoric acid or aqueous sulphuric acid (50 vol. %); it was found, however, that di*cyclo*pentadiene polymerises without evolution of gaseous *cyclo*pentadiene.

The catalysis by gaseous acetic acid was studied at 110° in the apparatus described by Benford and Wassermann (J., 1939, 362). In a typical experiment the acetic acid pressure was 168·0 mm. of mercury and the initial pressure of *cyclo*pentadiene was 334·5 mm. After 350 mins. the pressure decrease was 22·0 ± 1 mm. both in the empty and in the packed reaction vessels; in a control experiment without acetic acid vapour the pressure decrease was 14 ± 1 mm. The products of several catalytic experiments were collected and jointly redistilled; there was no indication that polymeric *cyclo*pentadiene was formed.

Reaction (*V*).—Rate measurements were carried out by shaking 50 c.c. of the reaction mixture containing 3 g. of finely powdered tetrachlorobenzoquinone in a dark thermostat; after known time intervals, the solvent was evaporated at room temperature and under reduced pressure, and the purified product weighed. The results of typical experiments at 25° are in Table VI. The catalytic effect of trichloroacetic acid obtains also at 21°, 29°, and 36° and in solutions which were 0·34—1·3M with respect to *cyclo*pentadiene and 0·002—0·05M with respect to the acid; in all these runs the tetrachlorobenzoquinone was not completely dissolved at zero time.

TABLE VI.

Catalysis of the formation of cyclo*pentadiene–tetrachlorobenzoquinone—typical experiments.*

	Concn., g.-mols./l.			Reaction, %.	
Catalyst.	C_5H_6 initially.	Catalyst.	Time of reaction, mins.	Without catalyst.	With catalyst.
$CCl_3 \cdot CO_2H$	0·65	0·0100	1400	20	72
NMe_3	0·65	0·0100	1400	20	58

A rate-accelerating influence of trimethylamine with simultaneous illumination by sunlight has been described by Albrecht (*Annalen*, 1906, **348**, 45), who omitted, however, to carry out control experiments in the dark. He did not establish, therefore, whether a thermal or a photochemical catalysis of reaction (V) takes place.

UNIVERSITY COLLEGE AND IMPERIAL COLLEGE, LONDON.

[*Received, August 6th*, 1942.]