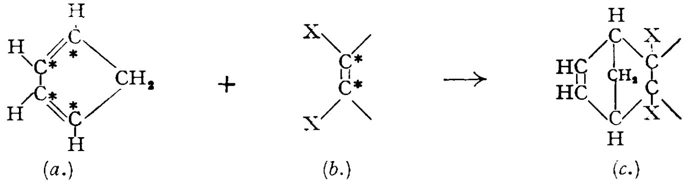
455. *Kinetics of the* cyclo*Pentadiene–Chloranil Reaction. A Note on the Configuration of Transition States in Diene Synthesis.*

By W. Rubin and A. Wassermann.

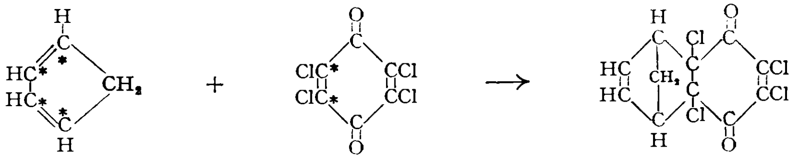
The results of kinetic measurements make it probable that in a reactive collision of Diels–Alder diene associations the diene and the dienophile take up a mutual orientation in which six specified carbon atoms, including the four reactive centres, are not situated in one and the same plane.

In previous papers of this series (Wassermann, *J.*, 1935, 828; 1936, 1028) the kinetics of bimolecular associations of the following general type have been studied, the substituent X being hydrogen in all cases:



(1)

The experiments now to be described deal with the bimolecular addition of *cyclo*pentadiene to chloranil which is formulated as shown below (see Alder, Abderhalden's "Handbuch der Biologischen Arbeitsmethoden," 1933, Abt. I, Teil II, 2. Haelfte Bd. II, p. 3110):



(2)

This diene synthesis is of the same type as (1) but the substituent X is chlorine. It has been found that the kinetic parameters *A* and the activation energies *E* of (1) are not markedly different from the corresponding values of (2); and, based on these observations, an attempt is made to draw certain conclusions on the steric configuration of the transition state of these Diels–Alder diene synetheses.

Experimental.—The molar extinction coefficient, β,* of carefully purified chloranil in benzene solution is 15·9 ± 0·3 l. g.-mol.$^{-1}$ cm.$^{-1}$ for light of 4700 A. Beer's law was tested in the range 0·002—0·04 g.-mol./l. (20°) and found to be valid. The rate of (2) is so slow that the light absorption of mixtures of chloranil and *cyclo*pentadiene could be measured before any appreciable formation of the addition product had occurred; and it was established that the addition of *cyclo*pentadiene gives rise to an increase of β. The effect is shown in Fig. 1, the graph relating to a chloranil concentration of 0·0200 g.-mol./l.

Other measurements showed that Beer's law holds for each *cyclo*pentadiene concentration specified in the figure; further, *cyclo*pentadiene–chloranil, the product of (2), is practically colourless, and, therefore, the rate of this diene association can be measured by the same colorimetric technique as that described in our earlier paper (1935, *loc. cit.*). In order to obtain reproducible results, the reaction mixture must be kept in the dark, except during the relatively short periods when light absorption measurements are actually performed. Exposure of mixtures of *cyclo*pentadiene and chloranil for longer times to light of high intensity (*e.g.*, daylight) gives rise to the development of a deep red coloration.

Table I.

Addition of cyclo*pentadiene to chloranil in benzene solution at* 60·0°. (Initial concn. of reactants, 0·0378 g.-mol./l. Thickness of absorption cell, 0·500 cm.)

Time (hours)	0	2·2	5·7	10·2	24·0
Drum reading (Filter S 47)	46·3	54·1	63·7	69·5	81·0 *
k(l. g.-mol.$^{-1}$ hr.$^{-1}$)	—	2·7	3·0	2·8	2·9

* At this stage 70% reaction has taken place.

Typical results of the kinetic measurements are in Table I, and a summary of the experiments is in Table II. The validity of Arrhenius's equation $k = Ae^{-E/RT}$ is shown in Fig. 2; the parameters *A*

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* $\beta = (1/dc) \log_{10} I_0/I$, where *d* is the thickness of the absorption cell, *c* the concentration, and I_0 and *I* are the intensities of the incident and the transmitted light.

and *E* relating to the addition of *cyclo*pentadiene to chloranil are in the first line of Table III, the other figures relating to the previously investigated reactions of the type (1) (Wassermann, *locc. cit.*).

TABLE II.

Addition of cyclo*pentadiene to chloranil in benzene solution : Summary of kinetic measurements.*

Temp.	Initial concn. of reactants (g.-mol./l.). C_5H_6.	$C_6Cl_4O_2$.	*k* (l. g.-mol.$^{-1}$ hr.$^{-1}$).
10·0°	0·0378	0·0378	0·049 ± 0·005
25·0	0·0378	0·0377	0·25 ± 0·03
	0·0756	0·0189	0·25 ± 0·03
	0·0378	0·0189	0·25 ± 0·03
	0·00940	0·00940	0·30 ± 0·05
40·0°	0·0378	0·0378	0·63 ± 0·1
	0·0189	0·0189	0·73 ± 0·05
60·0	0·0378	0·0378	2·8 ± 0·2

TABLE III.

Kinetic A *factors and activation energies,* E, *of diene associations of the type represented by* (1). (All results relate to benzene as solvent.)

Reactant (*b*).	Substituent X.	$\log_{10} A$ (*A* in l. g.-mol.$^{-1}$ sec.$^{-1}$).	*E* (kcals.).
Chloranil	Cl	6·2 ± 0·5	14·5 ± 0·5
Benzoquinone	H	6·5 ± 0·4	11·6 ± 0·6
α-Naphthaquinone	H	4·8 ± 0·9	10·0 ± 1·0
*cyclo*Pentadiene–benzoquinone ...	H	5·5 ± 0·9	13·2 ± 1·0
Acraldehyde	H	6·1 ± 0·3	13·7 ± 0·5
*cyclo*Pentadiene	H	6·1 ± 0·4	16·4 ± 0·6

Discussion.—During a reactive collision of the diene and the dienophile in reactions (1) or (2) two types of mutual orientation are of interest. In the first mode of addition these reactants approach each other in such a way that the six carbon atoms, indicated by asterisks, are situated in one plane, such collisions being conducive for the formation of "planar" transition states. In the alternative type of addition the reactants move towards each other in different planes as schematically represented elsewhere (Wassermann, *J.*, 1935, p. 1512, Fig. 1; *Trans. Faraday Soc.*, 1939, **35**, 841), thereby giving rise to "non-planar" transition states of a steric configuration somewhat similar to that of the fully formed product molecules. In the formation of the planar transition states the required juxtaposition of four carbon atoms can only be brought about if a considerable steric hindrance is overcome, this being due, *inter alia*, to interaction between the diene and the substituent X of the dienophile. Steric effects should be relatively large in reaction (2) because here the atomic radius of X is larger than in the associations of type (1).* If, therefore, planar transition states played a rôle, one would expect that either the non-exponential *A* factor of the Arrhenius equation or the activation energy, *E*, or both, would change markedly on passing from the reaction in which X is chlorine to one in which X is hydrogen. It will be seen, however, that all the *A* factors in col. 3 of Table III agree within the limits of the experimental errors. The activation energies show a moderate variation, and there can be no doubt that the *E* value of the chloranil reaction is at least 2—3

FIG. 1.

Influence of cyclo*pentadiene on molar absorption coefficient of chloranil in benzene (room temp.;* 4700 A.).

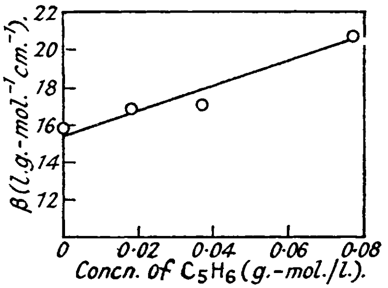
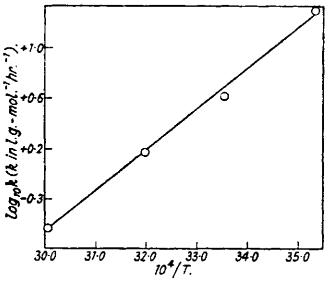


FIG. 2.

Validity of Arrhenius equation in reaction (2).



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* The ratio nuclear separation C–Cl/nuclear separation C–H is about 1·6.

kcals. larger than that of the associations involving benzoquinone or α-naphthaquinone; there is no evidence, on the other hand, that the activation energies listed in the last three lines of Table III are smaller than the value in the first line. It appears therefore, that on the whole the activation energy is not fundamentally dependent on the nature of the substituent X. This can be regarded as evidence against the assumption that planar transition states play a rôle in these reactions. The observations are compatible, however, with the alternative mode of addition; for it is obvious from simple considerations of models that steric effects should be less important if the reactants approach each other in different planes, thereby enabling the close proximity of the four reactive centres without considerable interaction between the substituent X and a number of atoms of the diene molecule.

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