204. *Stereochemical Factors in the Kinetics of Diels–Alder Associations.*

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The activation energies, E, of two Diels–Alder syntheses involving butadiene are larger than the E values of similar associations in which *cyclo*pentadiene is one of the reactants. This is explained by the fact that the double bonds of the open-chain and the cyclic diene are respectively in the *trans*- and the *cis*-position relative to each other.

Buta-1 : 3-diene is a mixture of *cis*- and *trans*-isomers, the latter predominating at temperatures below 300° (Aston, Szasz, Wooley, and Brickwedde, *J. Chem. Physics*, 1946, **14**, 67; Aston, *Discuss. Faraday Soc.*, 1951, **10**, 73), whereas the conjugated double bonds of *cyclo*pentadiene are fixed in the *cis*-position. Owing to this stereochemical difference a kinetic comparison of second-order homogeneous Diels–Alder syntheses involving butadiene and *cyclo*pentadiene is of interest. Experiments have been carried out, therefore, dealing with the following association :

Butadiene + Benzoquinone = Adduct (benzene solution; rate constant $= k_1$; activation energy $= E_1$) . . . (1)

the activation energy of which is compared with that of the reaction :

*cyclo*Pentadiene + Benzoquinone = Adduct (benzene solution; rate constant $= k_2$; activation energy $= E_2$) . . . (2)

the latter being already known from previous work (Wassermann, *J.*, 1936, 1028). A further kinetic comparison is made between two dimerisations of the Diels-Alder type, *viz.*,

2-Butadiene = Adduct (gas phase; rate constant $= k_3$; activation energy $= E_3$) . (3)

2-*cyclo*Pentadiene = Adduct (gas phase; rate constant $= k_4$; activation energy $= E_4$) . (4)

which were investigated, within a comparable temperature range, by Kistiakowsky and Ransom (*J. Chem. Physics*, 1939, **7**, 725) and by Benford and Wassermann (*J.*, 1939, 363). The results of the experiments now to be described and those of the earlier work show that $E_1 > E_2$ and $E_3 > E_4$, and the purpose of this paper is to explain these observations.

Experimental and Results.—The buta-1 : 3-diene contained less than 1% of butenes (spectroscopically tested), and the total amount of impurities was less than 2%, as found by distillation and reaction with excess of molten maleic anhydride. Benzoquinone was recrystallised until the m. p. and the extinction coefficient at 4700 Å agreed with previously recorded values. Dried butadiene was slowly passed, at room temperature, through a trap fitted with ground joints and containing a known weight of benzene, solutions of known concentration being prepared by weighing the trap before and after the butadiene absorption. The solution could be transferred into a reaction vessel containing the required amount of benzoquinone without significant loss of butadiene. The kinetics of reaction (1), at 25·0°, were measured by determining colorimetrically the benzoquinone consumption, this technique (see *J.*, 1936, *loc. cit.*) being applicable because butadiene and the final adduct are colourless. The results of these measurements are in Table 1. At higher temperatures the colorimetric method is not sufficiently accurate because of loss of butadiene, and therefore a technique was worked out enabling a continuous observation of the vapour pressure of the reaction mixture, and thus of the butadiene content. These measurements were done by means of a mercury manometer to which a reaction vessel *A* could be attached by means of standard joints and spring clips. Vessel *A* containing the benzoquinone was in the first instance connected with the trap containing the butadiene solution, which was sucked over by cooling *A* with liquid air. After disconnection of the trap, *A* was quickly fitted to the manometer, and the system was thoroughly evacuated, while *A* was cooled to −190°, no attempt being made, however, completely to remove dissolved or occluded air from the frozen mixture. The manometer, together with *A*, was then placed in a thermostat (fitted with a glass window) the temperature of which was constant to within ±0·02°. The results of a typical run are in Table 2, and the mean values of the rate constants, k_1, determined at four temperatures, are in Table 3. The Arrhenius rate equation $k_1 = A_1 e^{-E_1/RT}$ is obeyed with $\log_{10} A_1 = 5{\cdot}2 \pm 0{\cdot}6$ (A_1 in l.mole^{-1} sec.$^{-1}$)

TABLE 1. *Kinetics of reaction* (1) *at* 25·0°; *colorimetric technique*; *benzene solution.*

Concn. (mole l.$^{-1}$) Butadiene	Concn. (mole l.$^{-1}$) Benzoquinone	Cell thickness (cm.)	Final conversion, %	k_1 * (l. mole^{-1} hr.$^{-1}$)
0·707	0·0105	4·00	87	0·0113 ± 0·008
0·330	0·00240	20·0	58	0·0107 ± 0·0008
0·0817	0·0817	0·500	29	0·0099 ± 0·0010

* Mean value of at least five observations.

TABLE 2. *Kinetics of reaction* (1) *at* 55·0°; *vapour-pressure technique*; *benzene solution.*

Equimolar initial concentrations of reactants = 0·867 mole l.$^{-1}$.

Time (hr.)	0	0·100	0·200	0·300	0·400	0·500	0·600	0·800	
Vap. press. (mm.) ...	676	673	670	667	664	662	659	653	
k_1 (l. mole^{-1} hr.$^{-1}$) ...	—	0·103	0·103	0·106	0·110	0·101	0·105	0·101	
Time (hr.)	1·00	1·50	2·10	2·80	3·60	4·30	5·60	6·50	∞
Vap. press. (mm.) ...	648·5	636·5	622	608	593	580·5	563·5	555	337
k_1 (l. mole^{-1} hr.$^{-1}$) ...	0·101	0·104	0·103	0·103	0·105	0·102	0·098	0·098	—

TABLE 3. *Rate constants*, k_1, *of reaction* (1) *in benzene solution.*

Temp.	25·0°	35·00°	45·00°	55·00°
Final conversion, %	29—87	60	31	27
k_1 (l. mole^{-1} hr.$^{-1}$)	0·0110	0·0210	0·0471	0·101

and an E_1 value listed in col. 4 of Table 4, which also contains the previously determined activation energies of reactions (2)—(4).

Discussion.—Two mechanisms for second-order homogeneous Diels–Alder associations have been suggested, involving transition states formed by collisions in which the closest approach between carbon atoms of the reactants occurs at one or at two positions. In the first mechanism (Kistiakowsky and Ransom, *loc. cit.*) the transition state is regarded as a diradical subsequently converted into the fully formed product, whereas in the alternative mechanism (Wassermann, *J.*, 1942, 612) the transition state is stereochemically similar to the associated species. The first mechanism does not offer an obvious explanation for the figures in the last column of Table 4, while the relatively large activation energies of the butadiene reactions can be accounted for in terms of the second mechanism. A transition state of the specified stereochemical requirements can not be produced by *trans*-butadiene, and, therefore, a preliminary endothermic reaction, leading to the less stable *cis*-butadiene has to take place, before the " one-step " addition to the dienophile can occur. Reactions (1) and (3) are regarded, therefore, as consecutive processes, namely

TABLE 4. *Activation energies of Diels–Alder associations involving butadiene and* cyclo*pentadiene.*

Reaction no.	Diene	Dienophile	Activation energy (kcal.)	Difference (kcal.)
1	Butadiene	Benzoquinone	$E_1 = 14{\cdot}5 \pm 0{\cdot}6$	$E_1 - E_2 = 2{\cdot}9 \pm 1{\cdot}2$
2	*cyclo*Pentadiene		$E_2 = 11{\cdot}6 \pm 0{\cdot}6$	
3	Butadiene	Butadiene	$E_3 = 23{\cdot}7 \pm 0{\cdot}5$	$E_3 - E_4 = 7{\cdot}0 \pm 1{\cdot}1$
4	*cyclo*Pentadiene	*cyclo*Pentadiene	$E_4 = 16{\cdot}7 \pm 0{\cdot}6$	

$$C_4H_6 \underset{k_t}{\overset{k_c}{\rightleftharpoons}} cis\text{-}C_4H_6 \text{ (equilibrium constant} = k_c/k_t\text{, heat change} = \Delta H) \quad . \quad . \quad . \quad (5)$$

followed by

$$cis\text{-}C_4H_6 + C_6H_4O_2 = \text{Adduct (rate constant} = k_6\text{, activation energy} = E_6) \quad . \quad . \quad (6)$$

$$cis\text{-}C_4H_6 + cis\text{-}C_4H_6 = \text{Adduct (rate constant} = k_7\text{, activation energy} = E_7) \quad . \quad . \quad (7)$$

Taking *cis*-butadiene as a reactive intermediate of relatively short life time and applying the stationary-state approximation with $k_t \gg k_6 \times$ [Benzoquinone] or $k_7 \times$ [*cis*-Butadiene], we can show that

$$k_1 = k_6k_c/k_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$k_3 = k_7(k_c/k_t)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

It can be assumed, for the present purpose, that neither the entropies of *cis*- and *trans*-butadiene nor the logarithms of the non-exponential factors of the Arrhenius expression, relating to k_1 and k_6 or k_3 and k_7, are significantly different. If this be accepted, it follows from (8) and (9) that

$$E_1 = E_6 + \Delta H, \text{ and } E_3 = E_7 + 2\Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

It could be suggested that in the over-all dimerisation of butadiene, the following step also plays a rôle

$$cis\text{-}C_4H_6 + trans\text{-}C_4H_6 = \text{Adduct (activation energy} = E_{11}) \quad . \quad . \quad . \quad . \quad (11)$$

Consideration of models shows, however, that the transition state of (7) is more closely packed than that of (11); this is of relevance because a theoretical treatment of *endo–exo*-isomerism in Diels–Alder associations led to the conclusion that more closely packed transition states are preferred (Wassermann, *J.*, 1935, 1511; 1936, 432; *Trans. Faraday Soc.*, 1939, **35**, 841) and it is reasonable, therefore, to postulate that $E_{11} - E_7$ is sufficiently large to exclude a significant contribution of (11), within the temperature range here considered. The ΔH of (5) being taken as 2·3 kcal. (Aston *et al.*, *loc. cit.*), it follows from the over-all activation energies actually measured, E_1 and E_3, in conjunction with (10), that $E_6 = 12{\cdot}2 \pm 0{\cdot}6$ kcal. and $E_7 = 19{\cdot}1 \pm 0{\cdot}5$ kcal. It will be seen, therefore, that the differences $E_6 - E_2$ and $E_7 - E_4$, *viz.*, 0·6 ± 1·2 and 2·4 ± 1·1 kcal., are either smaller or not substantially larger than the experimental errors of the measured activation energies.

These results are fully compatible with the " one-step " mechanism of Diels–Alder reactions (*J.*, 1942, *loc. cit.*), because the modes of addition of (6) and (2) or of (7) and (4) should be fundamentally similar.

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