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HIGH PRESSURE (4+2) CYCLODIMERISATION OF 2,3-DIMETHYL 1,3-BUTADIENE POSSIBLE COMPETITION BETWEEN CONCERTED AND STEPWISE MECHANISMS

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The study of the pressure dependence of the rate constant in the (4+2) cyclodimerisation of 2,3-dimethyl 1,3-butadiene reveals a possible competition between concerted and stepwise mechanisms.

Despite extensive and argumented investigations, the exact temporal sequence of the bond formation in (4+2) cycloadditions remains to be determined [1]. Until recently, two main mechanisms have been considered : the pure concerted (no intermediates) and the stepwise processes (sequential formation of the two new bonds with a second lower energy barrier giving rise to a reaction intermediate : biradical or biradicaloid). Recently a third possibility has been introduced by Dewar [2] consisting in a two-step or two-stage mechanism where the rate-determining step is the conversion of the intermediate to the cyclic product, rather than its formation.

Early speculation on the mechanism focused on several chemical and theoretical arguments. It is not the aim of this short paper to revisit the various procedures, nevertheless it must be pointed out that the location of the transition state in the Diels-Alder reaction is difficult, even impossible to determine correctly by available experimental techniques. It is therefore necessary to calculate it by elaborate mathematical procedures [2,3] or to investigate it by dynamic methods [4] (determination of activation parameters). From this point of view, the method of the pressure dependence of the reaction rate yielding the activation volume may be a valuable one to distinguish, under certain conditions [5], both mechanisms, since the reaction coordinate is ultimately defined by the nuclear positions, so that the partial molar volume of reactants and transition state is more closely related to the reaction coordinate than any other variable.

The method has been applied by several authors to many Diels-Alder reactions and is now well documented [6]. They found invariably that for a given reaction, the activation volume $\Delta V^{\neq}$ is very close to the overall reaction volume ΔV . However, when scrutinizing the nature both of the diene and of the dienophile in these reactions, one may observe that in nearly all the diene and the dienophile behave as good donor-acceptor partners. It is a well-known fact that concerted cycloaddition transition states will be favoured over biradicaloid ones to a large extent for such complexes [7].

However the situation may change in cycloadditions of similar non-polar dienes to non-polar alkenes. Several years ago, we investigated the high pressure Diels-Alder dimerisation of 2-methylbutadiene (MB) [8] and found values for $\Delta V^{\neq}$ such as $\Delta V^{\neq} \simeq 0.9$ ΔV in the temperature range (40-70°C). We concluded that, even for reactants of low polarity, the transition state is product-like and the degree of concertedness very high. The same conclusion was drawn by Doering [1] in the dimerisation of butadiene, though on another basis.

TABLE 1

Pressure effect on the rate of the (4+2) dimerisation of DMB (a,b)

Pressure (c) (bar)	Rate constant 10^9 k $(l.M^{-1}s^{-1})$	k_p/k_1
1	0.41	1
390	0.63	1.54
735	0.82	2.00
980	1.13	2.76
1470	1.65	4.02
1960	2.16	5.27
2450	2.95	7.20
2940	4.0	9.8
5000	9.9	24.1

(a) T = 70,0°C, solvent (1-bromobutane)

(b) The experimental procedure was essentially the same as earlier described [8]. Kinetic measurements were made by GC (same conditions as in ref.8) the corrective factor of the dimer respective to solvent (used as standard) is 0.810

(c) Pressure is given to ± 5 bar, except in the upper region (± 30-40 bar). The rate constant is determined to within 2-3 %

We consider here a more crowded diene than MB : 2,3-dimethyl 1,3-butadiene (DMB). We obtained only the expected six-membered compound which was characterized by elemental and spectroscopic analysis. No trace of any cyclobutane derivative could be detected, indicating only (4+2) cycloaddition occurence. Table 1 shows the kinetic results obtained in the (1-5000 bar) region.

Tangential treatment of the curve Ln k = F (P) at zero pressure as well as Elyanov's mathematical procedure [9] give following values for $\Delta V^{\ddagger}$

$(\Delta V^{\ddagger})_{\text{graphical}} = -33.0 \pm 2.0$

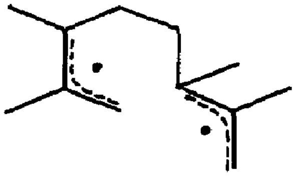
$(\Delta V^{\ddagger})_{\text{calculated according to ref. 9}} = -34.5$

$(\Delta V^{\ddagger})_{\text{calculated from a third degree polynomial (ref.8)}} = -33.0$

$(\Delta V)_{\text{experimental (by pycnometry)}} = -44.9 \pm 0.2$

All values are given in cm^3/mole at 70.0°C

Thus the activation volume represents about 70-75 % of the reaction volume and deviates from the usual values [6]. The data indicate that the distances between atoms participating in bond formation are not close to the interatomic distances in the adduct, so that the concertedness can be questioned. In a one-step concerted mechanism, both bonds are formed in the transition state although one cannot say whether partial formation of one bond is farther advanced than the other. However the present $\Delta V^{\ddagger}$-value can also be accounted for by the operation of a diradical (or a diradicaloid) intermediate, coexisting with the concerted mechanism :



Such species would be more stabilized than the corresponding ones for MB. Then, if a stepwise mechanism partially competes, the activation energy must be higher than in the cyclodimerisation of MB. From a temperature study, we deduce :

$$\Delta H^{\ddagger} = 25.4 \text{ kcal/mole} \quad \text{and} \quad \Delta S^{\ddagger} = -28.4 \text{ cal/d°mole}$$

(The corresponding values for the cyclodimerisation of MB at 70.0°C are $\Delta V^{\ddagger} = -42\ cm^3$/mole, $\Delta H^{\ddagger} = 18.9$ kcal/mole, $\Delta S^{\ddagger} = -41$ cal/d°mole)

The activation parameters of the dimerisation of DMB are compatible with the $\Delta V^{\ddagger}$-value and also may give support to the participation of a non-concerted mechanism.

We therefore consider as possible that both mechanisms compete in the (4+2) cyclodimerisation of 2,3-dimethyl 1,3-butadiene. However the applicability of the $\Delta V^{\neq}$-criterion to the present investigated reaction depends on the assumption that for the stepwise reaction the formation of the transition state preceding the intermediate is rate-controlling [10].

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