

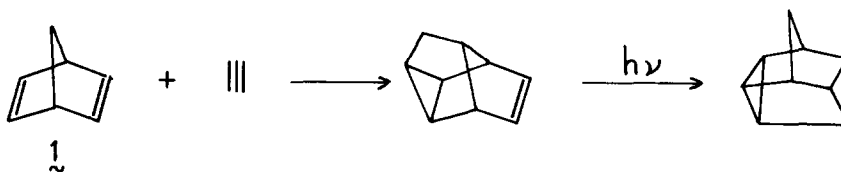
THE PRESSURE EFFECT IN THE HOMO-DIELS-ALDER REACTION (+)

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Summary. The homo-Diels-Alder reaction is accelerated by pressure to the same extent as Diels-Alder cycloadditions. On the basis of the activation volume, the establishment of the two new bonds is concluded to occur simultaneously.

The 1,5 addition of activated double or triple bonds to 1,4 dienes is known as the homo-Diels-Alder reaction discovered more than twenty years ago¹ and constitutes a useful reaction for the synthesis of peculiar bridged polycyclic compounds. The scope of the homo-Diels-Alder reaction was found as rather limited² for only bicyclo[2.2.1]hepta-2,5-diene is the most suitable (almost exclusive) homoconjugated diene, leading to deltacyclane derivatives (tetracyclo[4.2.1.0^{2,9}.0^{3,7}]nonanes) which in turn are starting candidates for bird-cage molecules via hv irradiation³.



The feasibility of the reaction was attributed to through-space interaction⁴ as shown in norbornadiene where ω has the optimum value⁵. When n and consequently ω increases, through-space interaction of the two diene moieties decreases.



Influence of solvent and pressure
on the kinetics of homo-Diels-Alder reactions (a)

Solvent	Solubility parameter (joule/mL) ^{1/2}	$10^6 k(\lambda + 2)$ at 90.2°C L.mol ⁻¹ s ⁻¹	$10^5 k(\lambda + 3)$ at 40.0°C L.mol ⁻¹ s ⁻¹
diethylether	30.10	1.27	-
toluene	37.20	-	4.08
benzene	38.04	4.64	8.88
acetone	40.13	3.54	-
dichloromethane	42.64	5.27	11.7
acetonitrile	49.32	3.64	17.2

Reaction	$\lambda + 2$ (solvent : benzene)	$\lambda + 3$ (solvent : toluene)	$\lambda + 3$ (solvent : acetonitrile)			
	P	10^6 k	P	10^5 k	P	10^4 k
ΔV_T^\ddagger (mL/mol) (b)	I	4.64	I	4.08	I	1.72
	180	6.29	260	5.92	290	2.36
ΔV_{25}^\ddagger (mL/mol) (b)	350	7.50	360	6.19	350	2.69
	540	8.85	540	7.61	440	3.18
ΔV_{25}^\ddagger (mL/mol) (c)	745	10.62	835	9.46	540	3.40
	1140	15.46	1140	13.60	835	4.13
	1930	23.03				
	-40.5 (± 1.5)		-30.0 (± 1.5)		-32.8 (± 2.0)	
ΔV_{25}^\ddagger (mL/mol) (b)	-31.5		-28.1		-30.8	
	-35.5		-32.9		-36.2	
$(\Delta V^\ddagger : \Delta \bar{V})_{25}$	0.89		0.85		0.85	

(a) Precision of rate constants k (2-3%) (ref. 10). Pressure is given in bar ($\pm 2-3$). The structure of the adducts was confirmed by IR and NMR and found to be similar to those described in the literature⁹.

(b) $\Delta V_T^\ddagger, \Delta V_{25}^\ddagger$: activation volumes at temperatures T and 25°C (ΔV_{25}^\ddagger was deduced from ΔV_T^\ddagger according to the procedure described in ref. 11).

(c) Reaction volume calculated from partial molar volumes of reactants and adduct (ref. 12).

Since two bonds are formed like in Diels-Alder reactions, the pressure effect should be particularly significant and characterized by high negative activation volumes⁶. However this is true only if the establishment of both bonds occurs simultaneously.

It is generally understood that the homo-Diels-Alder reaction proceeds via a six-membered ring transition state according to a thermally allowed three system ($\pi_s^2 + \pi_s^2 + \pi_s^2$) process, providing that the polarity of the reactants do not involve zwitterion intermediates⁷. However to our knowledge, no decisive argument has been proposed to sustain this assertion except two Japanese works reporting the retention of configuration in the reactions of norbornadiene with trans disubstituted dienophiles⁸.

The activation volume ΔV^\ddagger deduced from the response of the reaction rate to pressure may be indicative of the progression of the transition state. However to locate correctly the transition state, one should examine the absence of electrostriction throughout the reaction. As a matter of fact operation of electrostriction effects was found in the competitive $[2 + 2]$ vs $[2 + 2 + 2]$ reactions of tetrachlorobenzene with norbornadiene⁹.

As candidates for our reactions, we chose norbornadiene (1) and typical reactive dienophiles such as dimethyl acetylenedicarboxylate (2) and the more polar tetracyanoethylene (3), the reaction with the latter serving as an indicator of possible zwitterion intermediates. The table lists the kinetic results showing the solvent and the pressure effect.

The variations of the rate constant with solvent polarity is only minimal in both reactions : if the solubility parameter is chosen as the physical parameter of the solvent, the extreme ratio of rate constants is 4.1 (1 + 2) and 4.2 (1 + 3) from the least polar solvent to dichloromethane or acetonitrile. Such results are incompatible with the formation of dipolar intermediates in the transition state.

Activation volume data give strong evidence to this respect. The quasi-independence of ΔV^\ddagger on solvent polarity is a good argument precluding an ionic stepwise mechanism. Furthermore it may be observed that the $\Delta V^\ddagger : \bar{\Delta V}$ ratio is ≥ 0.85 , indicating a product-like transition state again arguing against any stepwise (diradical or ionic) process. Clearly the present results together with the previous regio- and stereospecificity results demonstrate that the homo-Diels-Alder reaction should be interpreted as a simultaneous bond forming non-polar process like ($\pi_s^4 + \pi_s^2$) cycloadditions.

Additionally it should be pointed out that the magnitude of ΔV^\ddagger for homo-Diels-Alder reactions allows substantial improvement of the yield, when the reactions are performed under high pressures. The synthetic aspect is currently under investigation.

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 1 : 103.2 (benzene) 103.4 (acetonitrile) 102.0 (toluene)
 2 : 123.3 (benzene)
 3 : 110.7 (acetonitrile) 105.4 (toluene)
 adduct ($1 + 2$) : 191.0 (benzene)
 adduct ($1 + 3$) : 174.5 (toluene) 177.9 (acetonitrile)

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