EFFECT OF PRESSURE ON THE CONROTATORY OPENING OF CYCLOBUTENES.
AN UNEXPECTED RESULT ?

Gérard Jenner

Laboratoire de Piézochimie Organique, Synthèse et Stéréoréactivité (UMR 7509),
Université Louis Pasteur, 1 rue Blaise Pascal, 67008 Strasbourg (France)

Abstract. Against intuitive expectation, conrotatory opening of cyclobutenes 1-4 is slightly promoted by pressure with activation volumes around - 2 to - 3 $cm^3.mol^{-1}$. The volume profile shows a minimum for the transition state TS. This result together with low activation entropy values demonstrates full concertedness and suggest a cyclic TS with a preferential orbital topology .
© 1998 Elsevier Science Ltd. All rights reserved.

Introduction

Electrocyclic reactions are processes involving the intramolecular cyclization of a n π electron system to a (n-2) π + 2 σ electron system or the reverse. The conrotatory electrocyclic opening of cyclobutenes has been a widely studied process both from a synthetic[1-3] and a theoretical[4-6] point of view. With respect to its clean stereochemistry, the reaction is the parangon for a nice demonstration of the Woodward-Hoffmann theory about conservation of molecular orbital symmetry[7]. In the framework of our studies devoted to the kinetic effect of pressure on pericyclic reactions[8], we became interested in electrocyclic reactions. Some time ago, we examined the cyclotautomerization process between norcaradiene and cycloheptatriene through a disrotatory electrocyclic reaction[9] . It was shown that the formation of norcaradiene products is largely promoted by pressure. Even the strong enophile diethyl azodicarboxylate which leads normally to the ene product at normal pressure, reacted under 900 MPa pressure in a [4+2] way yielding the diazene-norcaradiene adduct. An earlier study more related to the present work reported the ring opening of diphenylcyclobutenes under pressure (scheme 1)[10]. Negative $\Delta V^{\neq}$-values ($\Delta V^{\neq}$: activation volume) were found: - 12.5 (R = H) and - 7 $cm^3.mol^{-1}$ (R = CH_3). Such large values are rather unexpected and did not receive further justification. Intuitively, the rate constant should be retarded by pressure and hence, the reaction should experience a positive $\Delta V^{\neq}$ - value, since during the process, strain is released with twisting of the cyclobutane ring, stretching of the bridgehead bond and cleavage of a σ-bond. As the above reaction[10] was complicated by a parallel isomerization process and as the result remained isolated, we decided to look into such electrocyclic rearrangement reactions.

(*) Tel.: 33.03.88.41.68.15; Fax: 33.03.88.60.42.48; E-mail: jenner@chimie.u-strasbg.fr
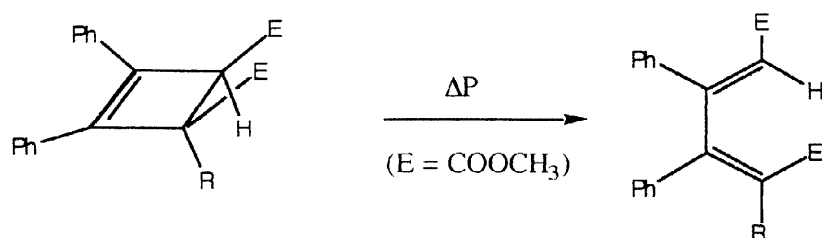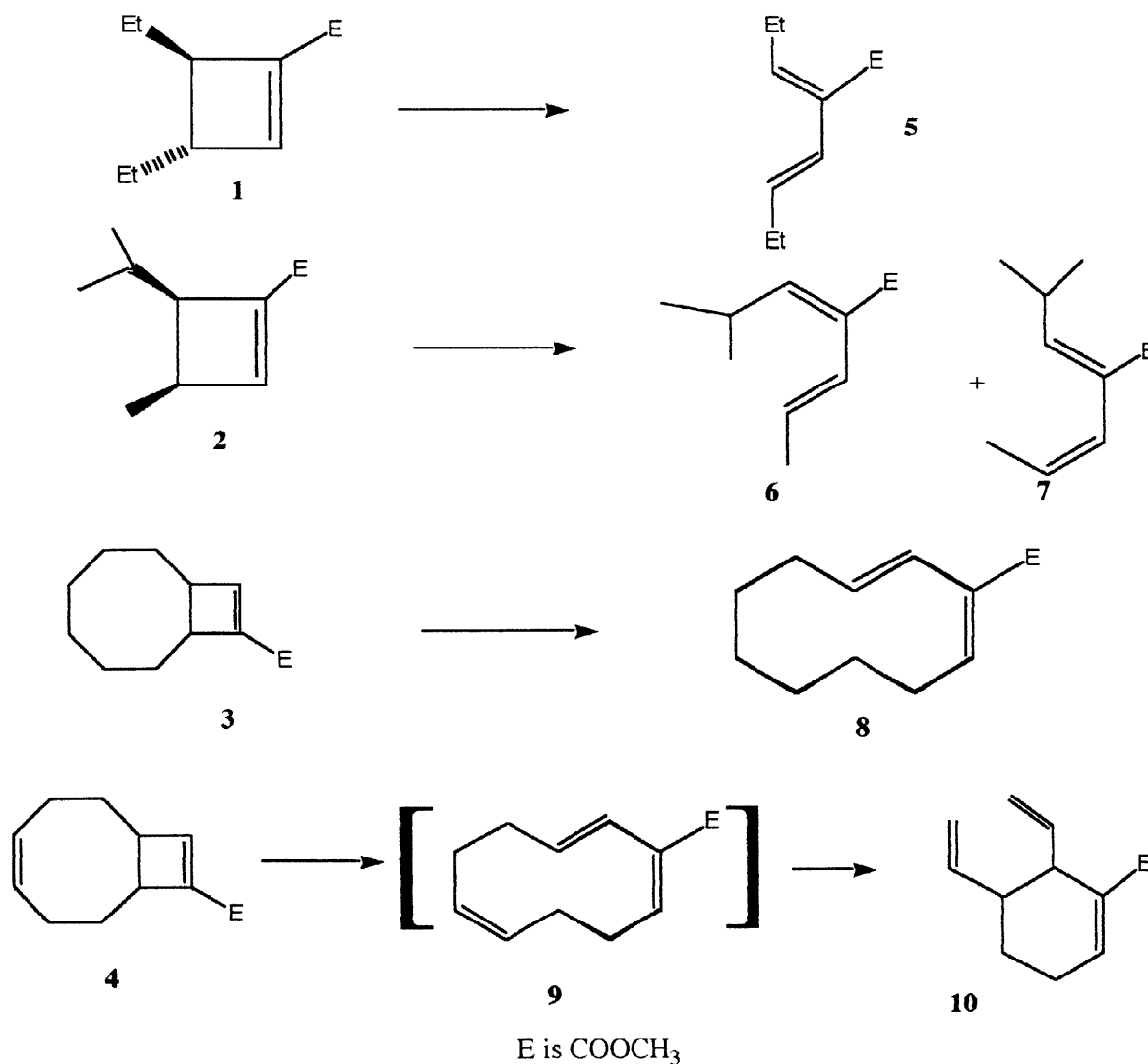
Scheme 1

Results

The substrates chosen were **1** and **2** as well as two annelated cyclobutenes **3** and **4** (scheme 2). Their rearrangement was previously examined at atmospheric pressure in the 140-200°C temperature range. In fact, the opening occurs already at lower temperature so that we were able to follow the kinetics with our home-made high pressure equipment, limiting the measurements below 110°C. Due to its dissymmetry, the rearrangement of **2** proceeds clockwise and counterclockwise leading to **6** and **7**. The opening of cyclobutene **4** presents an interesting particularity as the cyclodecatriene **9** is not isolated, but the product **10** resulting from a facile subsequent Cope rearrangement[11]. The kinetic results are listed in Table 1.

Table 1. Pressure kinetics of electrocyclic opening of cyclobutenes **1 - 4** (in CH_2Cl_2)

	$10^5 k\ (s^{-1})$			
T (°C) Pressure (MPa)	**1** 70.0	**2** 101.9	**3** 100.7	**4** 94.9
3	1.77	1.98	0.26	0.75
10	1.78	-	-	-
20	1.82	-	-	-
47	1.84	-	-	0.81
67	-	2.08	0.28	-
70	-	-	-	0.84
101	1.89	2.13	0.29	0.85
130	-	2.18	-	-
140	1.92	-	0.30	0.87
180	-	-	-	0.92
200	-	2.30	0.32	-
247	1.95	2.33	0.33	-
280	-	2.35	0.35	1.05
$\Delta V^{\neq}$ (± 0.5 cm^3.mol^{-1})	- 2.2	- 2.4	- 3.2	- 3.5

From the pressure dependence of rate constants the activation volume can be deduced. In the electrocyclic rearrangement of **4**, $\Delta V^{\neq}$ refers to the conrotatory opening process, although **9** is not observed. This is justified by the fact that, as **10** is the only isolated product, the Cope reaction is faster than the rearrangement of **4** to **9**.

Besides, it is well known that pericyclic sigmatropic processes are accelerated by pressure ($\Delta V^{\neq} \sim - 10$ to -20 $cm^3.mol^{-1}$)[12,13].

1

2

3

4

5

6

7

8

9

10

E is $COOCH_3$

Scheme 2

The important result is that the conrotatory opening of cyclobutenes is **promoted** by pressure, in agreement with the earlier result[10]. At first sight, the negative sign for $\Delta V^{\neq}$ is unexpected for such rearrangement. A seemingly similar situation was described in the retro-Diels-Alder reaction of a furan adduct[14] which underwent a slight pressure acceleration ($\Delta V^{\neq} \sim - 2\ cm^3.mol^{-1}$) despite the concerted cleavage of two σ-bonds. The result was rationalized by taking into account secondary orbital interactions contributing to the tightness of the transition state. By analogy, the retro-ene desulfination of an allylic sulfinic acid was also found to be accelerated by pressure[15]. The activation volume values found for the retro-Diels-Alder and retro-ene reactions are in fact quite understandable through the principle of microreversibility, since the forward reactions are characterized by $\Delta V^{\neq}$ - values lower than their respective reaction volumes[14,15].

Electrocyclic reactions were presented by Woodward and Hoffman[4] as processes in which conrotatory fission occurs concertedly with rehybridization of the concerned σ-orbitals or in other words, bonding interaction is maintained between the orbitals during the whole course of the reaction (the molecule has C_2 symmetry throughout the reaction) (Fig. 1). The orbital topology required for the electrocyclic process must be reflected in the $\Delta V^{\neq}$ - values. The negative value of the volume of activation is, therefore, related to a cyclic transition state retaining some ordering and refers at the evidence to a perfectly concerted process. The hypothesis of a slight electrostriction - which would make $\Delta V^{\neq}$ negative cannot be envisaged, since such electrocyclic reactions are isopolar.
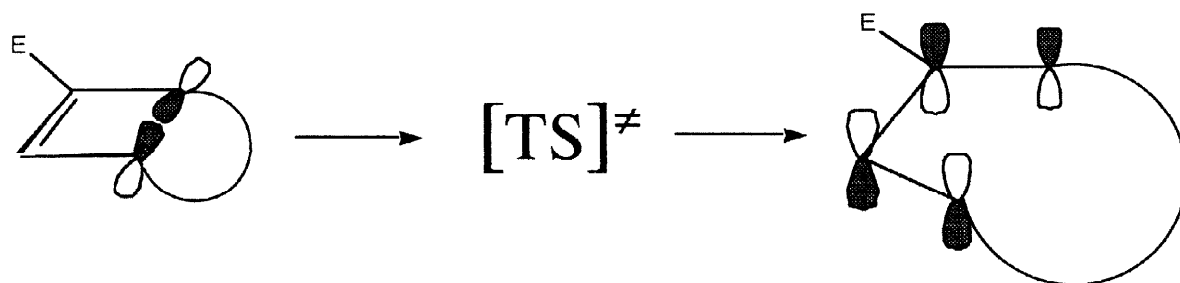
$$[TS]^{\neq}$$
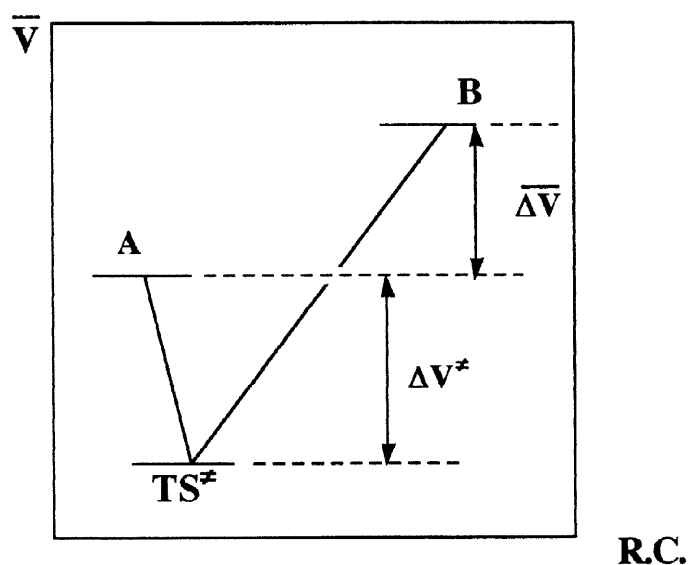
Figure 1. Electrocyclic opening of cyclobutenes

Figure 2. Volume profile of electrocyclic opening of cyclobutenes

The reaction volume is normally positive, since cyclic structures have higher densities than their open-chain analogs. We measured the reaction volume $\overline{\Delta V}$ (based on partial molar volumes of reactant and product) for the 3 → 8 rearrangement and found $\overline{\Delta V}_{25}$ = + 2.0 ± 0.5 cm^3.mol^{-1} (see experimental part). As a consequence, as $\Delta V^{\neq}$ is negative, the transition state is at a minimum in the volume profile (Fig.2). Although volumes of cyclization are ring size dependent, $\overline{\Delta V}$ > 0 is a common property of opening of cyclobutenes.

Such isomerization reactions should have relatively small entropies of activation[7]. This is supported by the $\Delta S^{\neq}$- values which we determined in the thermal rearrangement of 1 ($\Delta S^{\neq}$ ~ 8 J.mol^{-1}.K^{-1} and $\Delta H^{\neq}$ ~ 120 kJ.mol^{-1}) and 2 ($\Delta S^{\neq}$ ~ 0 J.mol^{-1}.K^{-1} and $\Delta H^{\neq}$ ~ 134 kJ.mol^{-1}). The entropy result can be compared to the

nearly zero value of $\Delta S^{\neq}$ in the thermal isomerization of Dewarbenzenes to benzenes which may be considered as a limiting case of the cyclobutene isomerization reaction[16]. Kinetic pressure studies involving the simple Dewar benzene and its hexamethyl analog were reported[17]. The $\Delta V^{\neq}$ - values were opposite in sign: + 5 and - 12 $cm^3.mol^{-1}$ respectively. However, in such case, the change of sign by saturating the ring with methyl substituents is probably related to the act of bringing all substituents in one plane (there is a pronounced increase in crowding when the molecule looses its dihedral structure to approach the flat geometry of the benzene ring, thus forcing the eclipse of all six methyl groups like a gear effect).

Conclusion

On the basis of the dramatic negative $\Delta V^{\neq}$- values observed for the conrotatory opening of cyclobutenes, the transition state is presumably featured by the requirement of a preferential orbital topology (direction of twisting) allowing the σ-framework to open in the most straightforward way. The rearrangements described in this paper experience full concertedness. However, the mechanistic ubiquity should be cautiously examined, since for more resistant annelated cyclobutenes (those having an adjacent five or six membered ring), the thermodynamic driving force may be ring strain[18], in such way that the conrotatory process becomes energetically disfavoured, suggesting either a concerted disrotatory opening or a biradical stepwise reaction[19].

The present pressure study complements nicely the understanding of the principles of electrocyclic reactions of cyclobutenes. At last, the results together with those characterizing (m+n) cycloadditions[8] and sigmatropies[12] are all consistent with concerted processes supported by the invariably negative $\Delta V^{\neq}$- values. This demonstrates amply the usefulness of the piezokinetic method for mechanistic delineation despite recent criticism[20].

Experimental part

Preparation of cyclobutenes. The cyclobutenes 1-4 were synthesized via [2+2] cycloadition of methyl propynoate to the corresponding alkene according to a procedure described earlier[21] and modified as follows: The acetylenic ester (1 eq.) was added to a dried CH_2Cl_2 solution of $ZrCl_4$ (0.5 eq.) under argon. After one hour stirring, the olefin (1.5 eq) was added dropwise and the mixture stirred at room temperature for 3-5 days under inert atmosphere. Work up is achieved by pouring the solution into a saturated sodium hydrogenocarbonate solution. The aqueous layer is washed twice with ether and the combined organic layers are washed with brine and dried over magnesium sulfate. After removal of solvent in vacuo, the residue was placed onto a silica gel column. Flash column chromatography (eluent: hexane-ether 9:1) yielded pure cyclobutenes in excellent yields.
Caution: Work up with $ZrCl_4$-propynoate complex may cause severe dermatis.

Kinetic measurements. For kinetic measurements, a CH_2Cl_2 solution of the required cyclobutene (5-7 $\times$ 10^{-2} $mol.dm^{-3}$) was introduced in a thick-walled stainless steel tube consisting of a cylinder and a piston fitted with a Viton ® O-ring and a steel ring. The extrusion of the piston due to the temperature in the vessel is prevented with the help of a stopping screw. The tube was immersed in the high pressure vessel whose temperature was controlled to at least 0.1°C and pressure to ± 0.5 MPa. After release of pressure, the reaction tube was immediately cooled. The solvent was removed in vacuo and the crude reaction products analyzed by ^1H NMR (200 MHz, $CDCl_3$). The spectra were in full agreement with those described in ref. 11 and 21.

Volume measurements. Precision density measurements permit the apparent molar volume Φ_V to be determined according to the known equation

$$\Phi_V = \frac{M_w}{d_0} - \frac{d - d_0}{d_0} \frac{1000}{C}$$

in which M_W is the molecular weight of the solute and C its molar concentration and where d and d_o are the densities of the solution and the solvent, respectively. Extrapolation of Φ_V to zero concentration gives the value of the partial molar volume. Density measurements were performed at 25.0°C in dichloromethane with a digital densimeter (Parr DMA 602). The partial molar volumes of **3** and **8** were respectively determined as : 177.8 and 179.8 $cm^3.mol^{-1}$. Accordingly, $\overline{\Delta V}_{25}$ has a value of + 2.0 ± 0.5 $cm^3.mol^{-1}$ which should approach 2.5-3 $cm^3.mol^{-1}$ at 101°C [22].

References

1. Durst T., Breau L., *Comprehensive Organic Chemistry*, Trost B. and Heathcock C., Eds., Pergamon Press, Oxford 1991), Vol. 5, 675-697

    Seebach D. in *"Houben-Weyl, Methoden der Organischen Chemie"*, Vol. 4, Part 4, G. Thieme Verlag, Stuttgart, 1971, pp. 414-421

2. Trost B.M., Mc Dougal P.G., J. Org. Chem., **1984**, *49*, 458-468

3. Binns F., Hayes R., Hodgetts K.J., Saengchantara S.T., Wallace T.W., Wallis C.J., Tetrahedron, **1996**, *52*, 3631-3658

4. Woodward R.B., Hoffman R., J. Am. Chem. Soc., **1965**, *87*, 395-397

5. Dauben W.G., Michno D.M., J. Am. Chem. Soc., **1981**, *103*, 2284-2292

6. Rondan N.G., Houk K.N., J. Am. Chem. Soc., **1985**, *107*, 2099-2111 and other papers cited

7. Dolbier W.R., Koroniak H., Houk K.N., Sheu C., Acc. Chem. Res., **1996**, *29*, 471-477

8. Jenner G., Bull. Soc. Chim. France, **1984**, 275-284

    Jenner G. in *"Organic High Pressure Chemistry"*, le Noble W.J. Ed., Elsevier, Amsterdam, 1988, p. 143-203

9. Jenner G., Papadopoulos M., J. Org. Chem., **1986**, *51*, 585-589

10. Mündnich R., Plieninger H., Tetrahedron, **1978**, *34*, 887-889

11. Radlick P., Fenical W., Tetrahedron Lett., **1967**, 4901-4904

12. Le Noble W.J., Daka M.R., J. Am. Chem. Soc., **1978**, *100*, 5961-5962

13. Degenerate Cope rearrangements may be non concerted : Schulman E.M., Merbach A.E., Turin M., Wedinger R., le Noble W.J., J.Am. Chem. Soc., **1983**, *105*, 3988-3991

14. Jenner G., M. Papadopoulos M., Rimmelin J., J. Org. Chem., **1983**, *48*, 748-749

15. Hiscock S.D., Isaacs N.S., King M.D., Sue R.E., White R.H., Young D.J., J. Org. Chem., **1995**, *60*, 7166-7169

16. Frey H., Walsh R., Chem. Rev., **1969**, *69*, 103-124

17. Le Noble W.J., Brower K.R., Brower C., Chang S., J. Am. Chem. Soc., **1982**, *104*, 3150-3152

18. Criegee R., Seebach D., Winter R.E., Börretzen B., Brune H.A., Chem. Ber., **1965**, *98*, 2339-2350

19. Frey H.M., Adv. Phys. Org. Chem., **1966**, *4*, 147-193

    Roth W.B., Rekowski V., Börner S., Quast M., Ann., **1996**, 409-430

20. Firestone R.A., Smith G.M., Chem. Ber., **1989**, *122*, 1089-1094

    Firestone R.A., Tetrahedron, **1996**, *52*, 14459-14468

21. Snider B.B., Rodini D.J., Conn R.S., Sealfon S., J. Am. Chem. Soc., **1979**, *101*, 5283-5293

22. El'yanov B.S., Vasylvitskaya E.M., Rev. Phys. Chem. Jpn, **1980**, *50*, 169-184