J. Am. Chem. Soc. **1994,** *116,* 7646–7657

Evidence for Pericyclic and Stepwise Processes in the Cyclodimerization of Chloroprene and 1,3-Butadiene from Pressure Dependence and Stereochemistry. Experimental and Theoretical Volumes of Activation and Reaction

Frank-Gerrit Klärner,*,† Bernd Krawczyk,† Volker Ruster,† and Ulrich K. Deiters*,‡

Contribution from the Institut für Organische Chemie, Universität GH Essen, Universitätsstrasse 5, D-45117 Essen, FRG, and Institut für Physikalische Chemie, Universität zu Köln, Luxemburger Strasse 116, D-50939 Köln, FRG

Received April 15, 1994●

Abstract: From the pressure dependence of cyclodimerization of chloroprene, it has been concluded that volumes of activation may be useful for the distinction between competing concerted and stepwise cycloadditions. Accordingly, one of the [4 + 2] cyclodimers, 1,4-dichloro-4-vinylcyclohexene (**4**), should be formed in a stepwise Diels–Alder reaction involving a diradical intermediate analogously to the [2 + 2] cyclodimerizations leading to *cis*- and *trans*-1,2-dichloro-1,2-divinylcyclobutane (**5** and **6**). A stereochemical analysis using (*E*)-1-deuteriochloroprene (**1**-D^{E}) shows, indeed, a nonstereospecific course for the formation of the formal Diels–Alder adduct **4** (*cis*:*trans* ratio of 59.6:40.4), as expected for a stepwise process, and confirms the conclusion drawn from pressure dependence. The mechanism of the Diels–Alder dimerization of 1,3-butadiene (**13**) is elucidated by an investigation of the effect of pressure and the stereochemistry. The activation volume found for the Diels–Alder dimerization leading to 4-vinylcyclohexene (**16**) turned out to be substantially lower than that found for the competing [2 + 2] cyclodimerization leading to *trans*-1,2-divinylcyclobutane (**17**) ($\Delta\Delta V^{*} = -13.3$ cm^3/mol). The dimerization of (*Z*,*Z*)-1,4-dideuterio-1,3-butadiene (**13**-1,4-D^{Z}) shows only 3% loss of stereochemistry in the formation of **16**-D at 1 bar and <1% at 6.8–8 kbar (*cis*:*trans* ratios of 97:3 and >99:<1, respectively). These findings provide good evidence for a stereospecific pericyclic Diels–Alder mechanism competing with a small amount of nonstereospecific stepwise reaction which is almost completely suppressed by high pressure. Volumes of activation and reaction are calculated for the Diels–Alder reaction of ethene with 1,3-butadiene (**13**) and the various dimerization pathways of 1,3-butadiene (**13**) by a Monte Carlo computer simulation using the model of hard spheres to describe the various ground and transition structures. The good agreement between calculated and experimental data shows that volumes of activation and reaction cannot be explained by properties of single molecules. They require consideration of configurational effects (e.g., the different packing of cyclic and acyclic states) for their interpretation. Thus, activation volumes can provide important information on transition-state geometries.

Introduction

Pressure in the range 5–20 kbar strongly influences the rate and position of equilibrium of many chemical reactions. Processes accompanied by a decrease of volume are accelerated by pressure (activation volume $\Delta V^{*} < 0$) while those accompanied by an increase of volume are retarded ($\Delta V^{*} > 0$).[1] Therefore, the application of high pressure seems to be particularly useful in controlling the course of competitive and consecutive reactions and can lead to an improvement of chemo-, regio-, and stereoselectivity.[2] Many Diels–Alder [4 + 2] cycloadditions show a powerful pressure-induced acceleration, which is often turned to good synthetic purposes.[3] The activation volumes ΔV^{*} resulting from the pressure dependence of the rate constants are usually highly negative ($\Delta V^{*} \approx -25$ to -45 cm^3/mol), sometimes even more negative than the corresponding reaction volumes ΔV ($\Delta V^{*}/\Delta V \approx 0.7$–$1.5$).[1a,b] Within the scope of the transition-state theory, activation volumes are considered to be a measure of the partial molar volume of transition states ($V^{*} = \Delta V^{*} - \sum V$ (starting materials)). Accordingly, the transition-state volumes of these reactions are close to or even smaller than the product volumes. This observation has been regarded as an indicator for a concerted mechanism of many Diels–Alder reactions.[2,4] In order to test this hypothesis and to gain further insight into the often more complex mechanism of Diels–Alder reactions, the investigation of the effect of pressure on competing [4 + 2] and [2 + 2] or [4 + 2] and [4 + 4] cycloadditions turned out to be advantageous for two reasons. First, the difference between the activation volumes and hence the transition-state volumes in competitive processes is derived directly from the pressure dependence of the product ratio. Second, in all the reactions listed in Table 1, the [2 + 2] or [4 + 4] cycloadditions doubtlessly occur in two steps via diradical intermediates and can, therefore, be used as internal standards of the activation volume required for a stepwise process. Thus, a relatively simple measurement of the pressure dependence of the product ratio should give important information about the mechanism of the Diels–Alder reaction.

In the thermal dimerization of chloroprene (**1**), the activation volumes of two [4 + 2] cycloadditions leading to **2** and **3** were found to be smaller than those of the third [4 + 2] and the [2

---

† Universität GH Essen.

‡ Universität zu Köln.

● Abstract published in *Advance ACS Abstracts,* July 15, 1994.

(1) Reviews: (a) Asano, Ti.; le Noble, W. J. *Chem. Rev.* **1978,** *78,* 407–489. (b) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989,** *89,* 549–688. (c) Buback, M. *Angew. Chem.* **1991,** *103,* 658–670; *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 641–653.

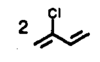
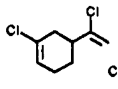
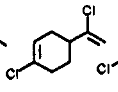
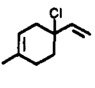
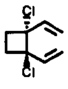
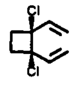
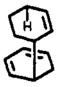
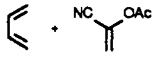
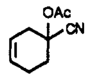
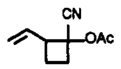
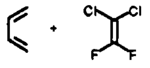
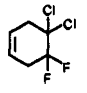
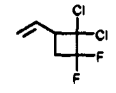
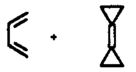
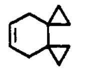
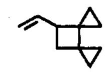
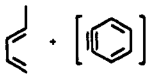
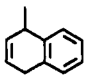
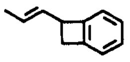
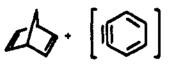
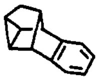
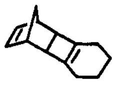
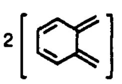
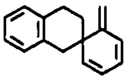
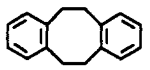
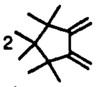
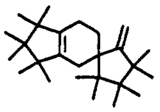
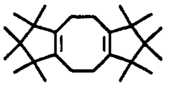
(2) Reviews: Klärner, F.-G. *Chem. Unserer Zeit* **1989,** *23,* 53–63. Klärner, F.-G.; Ruster, V.; Zimny, B.; Hochstrate, D. *High Pressure Res.* **1991,** *7,* 133–135.

(3) Reviews: (a) Matsumoto, K.; Sera, A.; Uchida, T. *Synthesis* **1985,** *1,* 1–26. Matsumoto, K.; Sera, A. *Synthesis* **1985,** *11,* 999–1027. (b) Jurczak, J. "*Synthesis*" *in Organic High Pressure Chemistry* le Noble, W. J., Ed.; Elsevier: Amsterdam, 1988; p 304–356. (c) Isaacs, N. S. *Tetrahedron* **1991,** *40,* 8463–8497. (d) *Organic Synthesis at High Pressure* Matsumoto, K., Acheson, R. M., Eds.; Wiley-Interscience: New York, 1991.

(4) Reviews: (a) Sauer, J.; Sustmann, R. *Angew. Chem.* **1980,** *92,* 773–801; *Angew. Chem., Int. Ed. Engl.* **1980,** *19,* 779–807. (b) le Noble, W. J.; Kelm, H. *Angew. Chem.* **1980,** *92,* 887–804; *Angew. Chem., Int. Ed. Engl.* **1980,** *19,* 841–856.

0002-7863/94/1516-7646$04.50/0

Table 1. Activation Volumes ΔV^{*}, Given in Parentheses, and Differences in Activation Volumes of Competing [4 + 2] and [2 + 2] or [4 + 4] Cycloadditions[a]

	reaction		[4 + 2] cycloadducts (ΔV^{*})	[2 + 2] or [4 + 4] cycloadducts (ΔV^{*})	$\Delta\Delta V^{*}$	ref
(1)	2  **1**	$\xrightarrow[1\text{-}10000\text{bar}]{23°\text{C}}$	 **2** (-31)  **3** (-29)  **4** (-22)	 **5** (-22)  **6** (-22)	-9 -7 0	5
(2)	2  **7**[b]	$\xrightarrow[1\text{-}7000\text{bar}]{70.5°\text{C}}$	 **8** (-28)  **9**[c] (-32)  **10** (-22)	 **11** (-18)  **12** (-22)	-10[d] -14[e] 0[f]	6
(3)		$\xrightarrow[1\text{-}9000\text{bar}]{80°\text{C}}$			-11.5	2,7
(4)		$\xrightarrow[1\text{-}10000\text{bar}]{80°\text{C}}$			0	2,8
(5)		$\xrightarrow[1\text{-}7000\text{bar}]{100°\text{C}}$			-2	2,9
(6)		$\xrightarrow[1\text{-}4000\text{bar}]{40°\text{C}}$			0	2,10
(7)		$\xrightarrow[1\text{-}5800\text{bar}]{40°\text{C}}$			0	2,11
(8)	2 	$\xrightarrow[1\text{-}6800\text{bar}]{80°\text{C}}$			-5	2,12
(9)	2 	$\xrightarrow[550\text{-}9300\text{bar}]{79.1°\text{C}}$	 (-15.8)	 (-15.5)	-0.3	13

[a] $\Delta\Delta V^{*} = \Delta V^{*}[4+2] - \Delta V^{*}[2+2]$ or $\Delta\Delta V^{*} = \Delta V^{*}[4+2] - \Delta V^{*}[4+4]$ (all values in units of cm^3/mol). [b] The dimers of **7** can be divided into two stereochemical classes: (1) **8**, **9**, and **11** are formally derived from a racemic diradical intermediate and (2) **10** and **12** from the corresponding *meso* diradical. [c] [6 + 4]-ene reaction. [d] ΔV^{*}(**8**) − ΔV^{*}(**11**). [e] ΔV^{*}(**9**) − ΔV(**11**). [f] ΔV^{*}(**10**) − ΔV^{*}(**12**).

+ 2] cycloadditions leading to **4**, **5**, and **6**, respectively. Stewart[5] explained these results in terms of concerted Diels–Alder reactions competing with stepwise [2 + 2] cycloadditions. According to its larger (less negative) activation volume, the Diels–Alder adduct **4** should also be formed in a nonconcerted process. Similarly it can be concluded from the pressure dependence of the dimerization of 1,3-cyclohexadiene (**7**)[6] that the *endo*-Diels–Alder dimer **8** and the [6 + 4]-ene product **9** are formed concertedly while the *exo*-Diels–Alder adduct **10** and the [2 + 2] cyclodimers **11** and **12** arise via diradical intermediates. According to the activation volume data summarized in Table 1, the Diels–Alder reaction of 1,3-butadiene with α-acetoxyacrylonitrile (entry 3)[2,7] and the Diels–Alder dimerization of *o*-quinodimethane (entry 8)[2,12] fall into the same class as those discussed for **1** and **7**, while all other Diels–Alder reactions in Table 1 seem to occur in stepwise fashion.[2,8,10,11,13]

In this paper we respond to three concerns. First, in order to substantiate the conclusions concerning pericyclic and stepwise processes drawn from the difference between the activation volumes of competitive [4 + 2] and [2 + 2] or [4 + 4] cycloadditions, we have examined the stereochemical course of the dimerization of (*E*)-1-deuteriochloroprene (**1**-D^E). Second, in the dimerization of 1,3-butadiene (**13**), the effect of pressure on the competitive processes and the stereochemical course have

---

(5) Stewart, C. A., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 635–637.

(6) Klärner, F.-G.; Dogan, B. M. J.; Ermer, O.; Doering, W. von E.; Cohen, M. P. *Angew. Chem.* **1986**, *98*, 109–111; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 108–110.

(7) Little, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 4020–4022.

(8) Bartlett, P. D.; Schmeller, K. E. *J. Am. Chem. Soc.* **1968**, *90*, 6077–6082. Swenton, J. S.; Bartlett, P. D. *J. Am. Chem. Soc.* **1968**, *90*, 2056–2058.

(9) Kaufmann, D.; de Meijere, A. *Angew. Chem.* **1973**, *85*, 151–152; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 159–160.

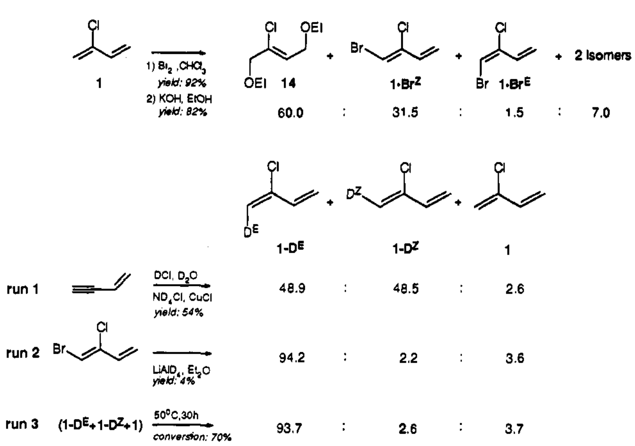
(10) De Camp, M. R.; Levin, R. H.; Jones, M., Jr. *Tetrahedron Lett.* **1974**, *40*, 3575–3578. Waali, E. E. *J. Org. Chem.* **1975**, *40*, 1355–1356.

(11) Simmons, H. E. *J. Am. Chem. Soc.* **1961**, *83*, 1657. Martin, H.-D.; Kagabu, S.; Schiwek, H.-J. *Tetrahedron Lett.* **1975**, *38*, 3311–3314.

(12) (a) Roth, W. R.; Scholz, B. P. *Chem. Ber.* **1981**, *114*, 3741–3750. (b) Bartmann, M. Zur Chemie des o-Chinodimethans und seiner Homologen. Pl.D. Dissertation, Ruhr-Universität Bochum, 1980 (Prof. Wolfgang R. Roth, Research Director). (c) Dogan, B. M. J. Organische Reaktionen unter hohem Druck; der Druckeffekt auf Konkurrenzreaktionen. Ph.D. Dissertation, Ruhr-Universität Bochum, 1984.

(13) Baran, J.; Mayr, H.; Ruster, V.; Klärner, F.-G. *J. Org. Chem.* **1989**, *54*, 5016–5019.

Scheme 1



been studied in order to elucidate the yet unresolved mechanism of the Diels–Alder dimerization leading to 4-vinylcyclohexene (**16**). Third, with the calculation of partial molar volumes starting from the van der Waals volumes of ground and transition structures using Monte Carlo simulation techniques, we have tried to understand the basic factors responsible for the observed differences in the activation volumes.

Stereochemistry of the Dimerization of Chloroprene: Synthesis and Thermolysis of (*E*)-1-Deuteriochloroprene (1-D^E)

Because the electrophilic addition of DCl to vinylacetylene[14] leads to a 1:1 mixture of (*E*)- and (*Z*)-1-deuteriochloroprene (**1**-D^E and **1**-D^Z), we examined if the reduction of (*Z*)-1-bromo-2-chloro-1,3-butadiene (**1**-Br^Z) with LiAlD$_4$ is a source of **1**-D^E. **1**-Br^Z could be prepared in the two steps starting from **1** shown in Scheme 1. Contrary to the literature,[15] we have assigned the structure of **1**-Br^Z to the major isomer from a comparison of the ^{1}H-NMR chemical shifts of 1-H^E and 1-H^Z with those of the corresponding hydrogen atoms in vinyl chloride and (*E*,*Z*)-1,4-dichloro-1,3-butadiene, where the assignment is unambigous due to the different olefinic coupling constants ($^3J_{cis} < {}^3J_{trans}$). Further details of this assignment are given in the Experimental Section. The reduction of **1**-Br^Z with LiAlD$_4$ occurred highly stereoselectively, leading to a 94.2:2.2:3.6 mixture of **1**-D^E, **1**-D^Z , and **1**. As shown in Figure 1, the product ratio could be easily analyzed in the 400-MHz ^{1}H-NMR spectrum, where the chemical shifts of 1-H^E{D^Z}, 1-H^E{H^Z}, 1-H^Z{H^E}, and 1-H^Z{D^E} were almost baseline separated from one another.

The thermolysis of **1** and **1**-D^E at 50 °C and 1 bar in the presence of catalytic amounts of bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide (BHMPS), which turned out to be a superior inhibitor against radical-chain polymerization of chloroprene, leads to the dimers already reported by Stewart.[5] The product ratio analyzed by GC is given in Table 2. The desired [4 + 2] and [2 + 2] cyclodimers **4**, **4**-D and **5**, **5**-D expected from the activation volume data to be formed via stepwise mechanisms, as well as the recovered starting material **1**, **1**-D^E, were isolated by preparative GC. The deuterium distribution in recovered **1**-D^E as analyzed by ^{1}H-NMR spectroscopy remained unchanged (Figure 1). In the ^{1}H-NMR spectrum (400 MHz, CDCl$_3$) of **4**, the six chemically nonequivalent *syn*- and *anti*-hydrogen atoms H^s and H^a at C-3, -5, and -6 (*syn* and *anti* relative to the vinyl group at C-4) show four signals in a 1:1:1:3 ratio (Figure 2). The signals at δ = 2.01 and 2.17 were assigned to the non-allylic hydrogen atoms 5-H^s and 5-H^a, respectively, and the remaining signals at δ = 2.36 and 2.6, to the allylic hydrogen atoms at C-3 and C-6. This assignment of 5-H^s, 5-H^a and 6-H^s, 6-H^a could be confirmed by homonuclear double resonance experiments. Irradiation of the resonance frequency assigned to 5-H^s or 6-H^s with a second rf field affected the disappearance of the large geminate coupling constant ($^2J_{a,s}$) in the corresponding signal of 5-H^a or 6-H^a. The assignment of 5-H^s to the signal at higher field is consistent with that of 1-H^E in the spectrum of **1**. In order to obtain the intensities of the signals as accurately as possible, the ^{1}H-NMR spectrum of **4**-D was recorded several times by using different delays of relaxation (0, 2, 4, and 6 s). From these measurements, the ratios of intensities can be calculated to be

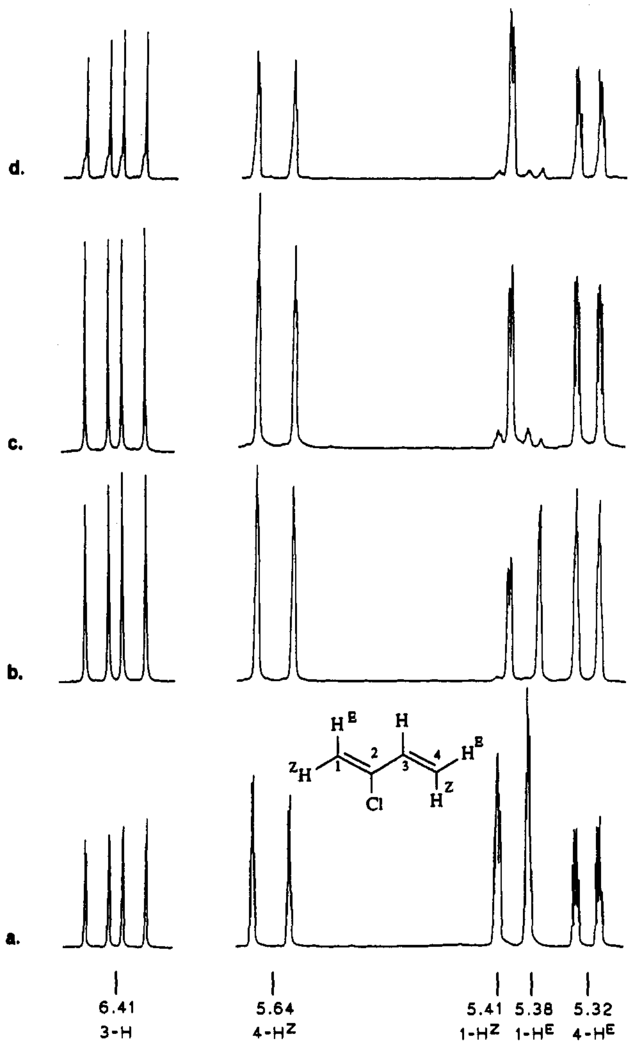


Figure 1. ^{1}H-NMR spectra (400 MHz, CDCl$_3$) of (a) **1**, (b) **1**-D^E + **1**-D^Z (Scheme 1, run 1), (c) **1**-D^E (Scheme 1, run 2), and (d) **1**-D^E recovered from the thermolysis of **1**-D^E at 50 °C, 30 h (Scheme 1, run 3).

Table 2. Product Ratio Determined by GC in the Dimerization of (a) Chloroprene (**11**)[a] and (b) (*E*)-1-Deuteriochloroprene (**1**-D^E)[b]

	product (product ratio (%))				
a	**2** (20.5)	**3** (15.4)	**4** (21.6)	**5** (23.6)	**6**[c] (18.9)
b	**2**-D (22.6)	**3**-D (15.8)	**4**-D (20.3)	**5**-D (22.9)	**6**-D[c] (17.6)

[a] 50% in toluene, 50 °C, 1 bar, 16 h, 40% conversion. [b] 50% in toluene, 50 °C, 1 bar, 30 h, 70% conversion. [c] Only 1,6-dichlorocycloocta-1,5-diene or 1,6-dichloro-7,8-dideuteriocycloocta-1,5-diene, respectively, as the product of a subsequent Cope rearrangement[5] of **6** or **6**-D was isolated under these conditions.

---

[14] (a) The addition of DCl to vinylacetylene was performed analogously to that of HCl: Carothers, W. C.; Williams, I.; Collins, A. M.; Kirby, J. E. *J. Am. Chem. Soc.* **1931**, *53*, 4203–4225. (b) Vinylacetylene was prepared according to the reported procedure: Karlsson, F.; Smith, Z.; *Acta Chem. Scand.* **1979**, *A33*, 483. Cederbalk, P.; Karlsson, F. *Acta Chem. Scand.* **1981**, *A35*, 7–11.

[15] Petrov, A. A. *J. Gen. Chem. USSR* 1943, 13, 108–112; *Chem. Abstr.* **1944**, *38*, 330. Petrov, A. A.; Babayan, V. O. *Zh. Obsch. Khim.* **1964**, *34*, 2633; *J. Gen. Chem. USSR* **1964**, *34*, 2654–2658.

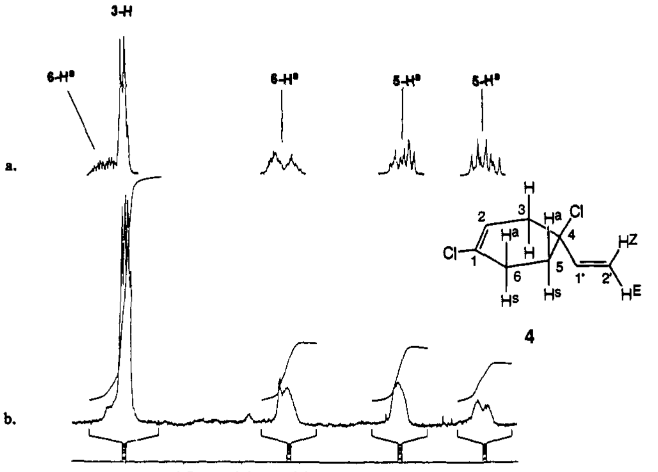
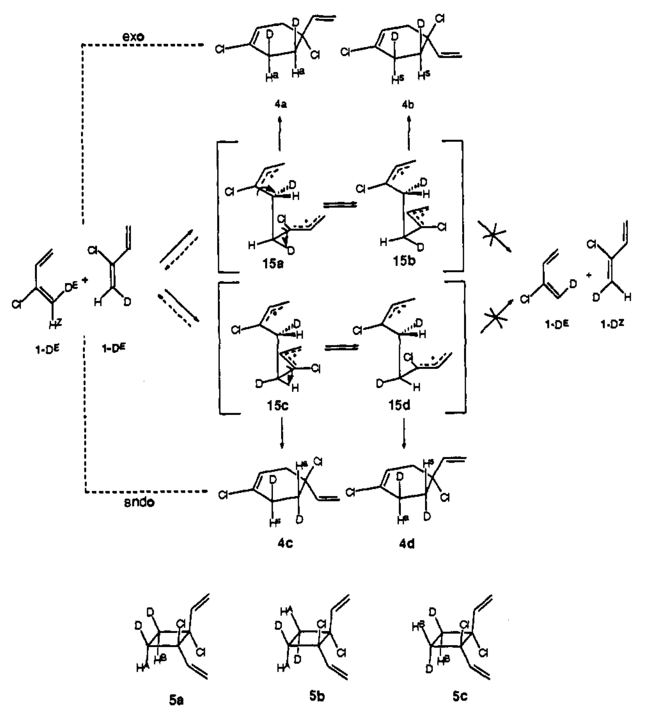


Figure 2. ^{1}H-NMR spectra (400 MHz, $CDCl_3$) of (a) **4** and (b) **4**-D isolated from the thermolysis of **1**-D^E at 50 °C for 30 h.

Scheme 2



$I(5\text{-H}^a):I(5\text{-H}^s) = (1.43 \pm 0.06)$ and $I(6\text{-H}^a):I(6\text{-H}^s) = (2.13 \pm 0.58)$ and hence the ratios of products [**4a** + **4c**]:[**4b** + **4d**] = 0.588:0.412 and [**4a** + **4d**]:[**4b** + **4c**] = 0.68:0.32.

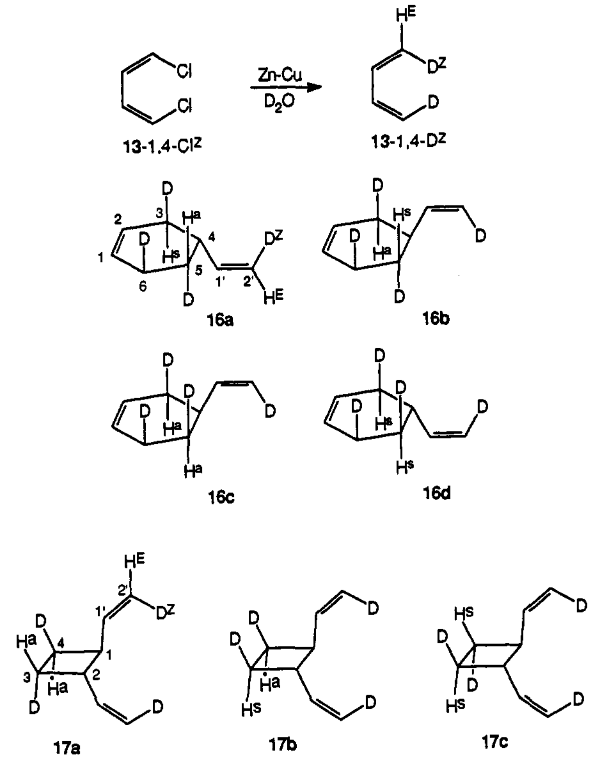
The deuterium distribution in the [2 + 2] cyclodimer **5**-D could be determined analogously. In the ^{1}H-NMR spectrum (400 MHz, $CDCl_3$), the *cis*-dideuterio adduct **5a** showing an AB spectrum for the chemically nonequivalent hydrogen atoms 3-H^A and 4-H^B (δ = 2.32, 2.77, $^3J_{AB}$ = 9 Hz) is cleanly distinguished from the two possible *trans*-dideuterio adducts **5b**,**c** which each show only one singlet for the chemically equivalent hydrogen atoms 3-, 4-H^A or 3-, 4-H^B in the center of each doublet stemming from **5a**. From the intensities of these signals, the product ratio was estimated to be[**5a**]:[**5b**]:[**5c**] = 0.48:0.34:0.18.

From the deuterium distribution reported above, the diastereomeric excess (de) in the Diels–Alder dimerization **21**-D^E → **4**-D can be calculated to be only:

$$\text{de} = ([\mathbf{4a} + \mathbf{4c}] - [\mathbf{4b} + \mathbf{4d}])/([\mathbf{1}\text{-D}^E] - [\mathbf{1}\text{-D}^Z]) = (0.588 - 0.412)/(0.942 - 0.022) = 0.191$$

This lack of stereospecifity provides clear-cut evidence that the Diels–Alder dimerization **21** → **4** proceeds stepwise, most likely passing through the diradical intermediates **15a**,**c**, in which the rotation about the C–C single bonds (e.g., **15a** ⇌ **15b** or **15c** ⇌ **15d**) effectively competes with the ring closures, leading to the vinylcyclohexene derivatives **4a–d**. If the concerted, pericyclic process alone had been operating, **4a**,**c** would have been the products of an *exo*- and *endo*-Diels–Alder addition.

Scheme 3



The [2 + 2] cycloaddition of **1**-D^E leading to the *trans*-divinylcyclobutanes **5a–c** turned out also to be nonstereospecific, as expected of a stepwise process. Finally, the observation that the deuterium distribution in the recovered starting material **1**-D^E remained unchanged during the reaction up to 70% conversion shows that the equilibrating diradical intermediates **15a–d** are not cleaved to chloroprene under these conditions. The stereochemical findings reported here fully confirm the conclusion drawn from the differences in the activation volume data. It follows that the activation volume seems to be a suitable tool for distinguishing between pericyclic and stepwise reactions. With the next example—the dimerization of 1,3-butadiene—we intend to show that an activation volume more negative than that of the corresponding stepwise process indicates a pericyclic reaction.

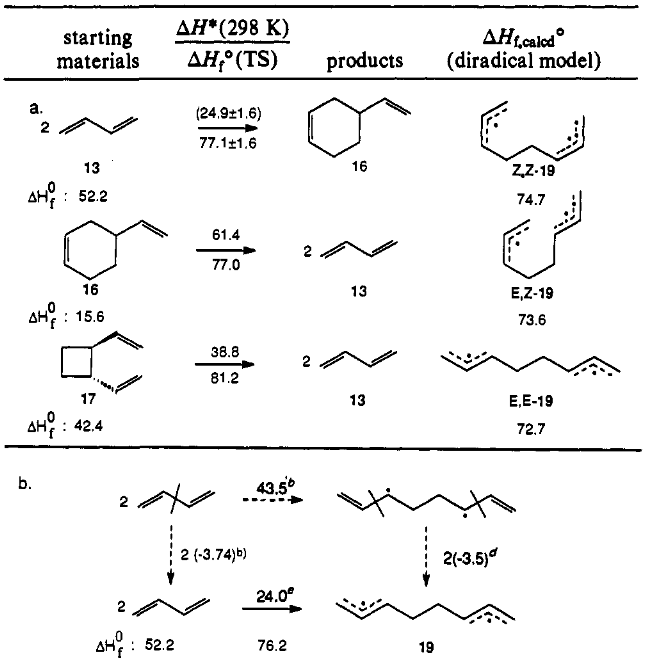
Pressure Dependence and Stereochemistry of the Dimerization of 1,3-Butadiene

In the dimerization of 1,3-butadiene, competition among [4 + 2], [2 + 2], and a formal [4 + 4] cycloaddition leads to 4-vinylcyclohexene (**16**), *trans*-divinylcyclobutane (**17**), and 1,5-cyclooctadiene (**18**), respectively.[16] Many studies have been undertaken to answer the question of whether the Diels–Alder product, 4-vinylcyclohexene (**16**), is formed in a pericyclic or

---

(16) (a) Ziegler, K.; Wilms, H. *Justus Liebigs Ann. Chem.* **1950**, *567*, 1–43. Read, H. W. B. *J. Chem. Soc.* 1951, 685. (b) Kinetic studies of the Diels–Alder dimerization of butadiene (**13**): Vaughan, W. E. *J. Am. Chem. Soc.* **1932**, *54*, 3863–3876. Kistiakowski, G. B.; Ransom, W. W. *J. Chem. Phys.* **1939**, *7*, 725–735. Rowley, D.; Steiner, H. *Discuss. Faraday Soc.* **1951**, *10*, 198–213. Huybrechts, G.; Luyckx, L.; Vandenboom, T.; Mele, B. *Int. J. Chem. Kinet.* **1977**, *9*, 283–293. (c) Pyrolysis of 4-vinylcyclohexene (**16**): Duncan, N. E.; Janz, G. J. *J. Chem. Phys.* **1952**, *20*, 1644–1645. Tsang, W. *J. Chem. Phys.* **1965**, *42*, 1805–1809. (d) Pyrolysis of *trans*-divinylcyclobutane (**17**): Hammond, G. S.; DeBoer, C. D. *J. Am. Chem. Soc.* **1964**, *86*, 899–902.

Table 3. Comparison between the Enthalpies of Formation of Transition States Derived from the Kinetic and Thermochemical Data of the Butadiene Dimerization[16b,c,d]



[a] $\Delta H_f°$(TS) = $\Delta H_f°$(starting material) + ΔH^*(298 K) and the enthalpies of formation $\Delta H_{f,calcd}°$ calculated for the diradicals **19** (a) by MM2ERW[18b] or (b) by a thermochemical estimate starting from the enthalpy of activation of the ethene dimerization[19] (all enthalpy values in kcal/mol). [b] Enthalpy of activation determined for the dimerization of ethene to cyclobutane. [c] Energies of conjugation between a pair of conjugated double bonds. [d] Allyl stabilization energy. [e] Calculated enthalpy of activation: $\Delta H^* = 43.5 + 2(-13.5) - 2(-3.74)$.

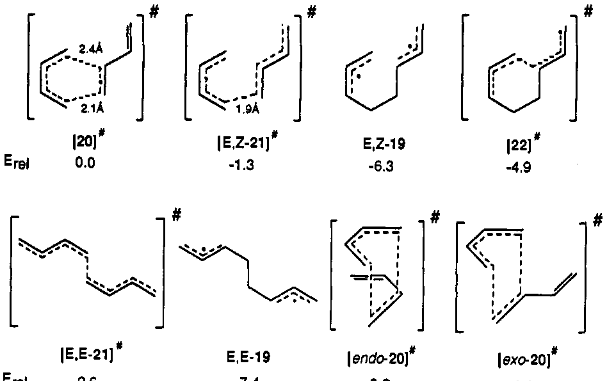


Figure 3. CASSCF/3–21G relative energies E_{rel} (kcal/mol) of transition structures and diradical intermediates determined by Li and Houk[20] for the butadiene dimerization.

stepwise process.[17] According to thermochemical estimates and the most recent quantum mechanical *ab initio* calculations, this reaction seems to be a borderline case. The enthalpies of formation derived for the transition states of the [4 + 2] as well as the [2 + 2] cycloaddition from the known kinetic and thermochemical data (Table 3) are close to or even higher than those calculated for the potential diradical intermediates (*Z,Z*-), (*Z,E*-), and (*E,E*)-**19** by using the force-field MM2ERW parametrized by Roth et al.[18] for the allyl radical. Doering, Belfield, and He[19] obtained similar results by estimating the activation enthalpy for the dimerization of 1,3-butadiene to the diradical **19** starting from the activation enthalpy of the dimerization of ethene to cyclobutane (Table 3b). In their *ab initio* study, Li and Houk[20] also predict the stepwise mechanism to be slightly favored, by 1.3 kcal/mol, over the pericyclic pathway (Figure 3). A stereochemical study reported by Stephenson, Gemmer, and Current[21] for the dimerization of (*Z,Z*)-1,4-dideuterio-1,3-butadiene showed 10% loss of stereochemistry in the formation of the 4-vinylcyclohexene. This finding led them to conclude that there is competition between orbital-symmetry-allowed [$\pi^4{}_s + \pi^2{}_s$] and forbidden [$\pi^4{}_s + \pi^2{}_a$] cycloadditions. But, the stepwise mechanism involving a diradical intermediate might also account for the partial loss of stereochemistry. Berson and Malherbe,[22] however, observed a stereospecific Diels–Alder dimerization of the related (*E,E*)-1-deuterio-1,3-pentadiene.

Increasing pressure enhances the overall rate of dimerization of 1,3-butadiene and shifts the product ratio further toward 4-vinylcyclohexene (**16**). Activation volumes (ΔV_0^*) are obtained from the pressure dependence of the overall rate constant of dimerization and the product ratio measured at 119.8 °C by GC. Reaction volumes (ΔV_R) are calculated from the partial molar volume of starting materials and products in the usual manner[1] (general chemical reaction: $\nu_{E_1}E_1 + \nu_{E_2}E_2 + ... \rightarrow \nu_{P_1}P_1 + \nu_{P_2}P_2 + ...$; $\Delta V_R = \sum \nu_{P_i}V_{P_i} - \sum \nu_{E_i}V_{E_i}$). The partial molar volumes (V_{E_i} or V_{P_i}) are determined by measuring the concentration-dependence of the densities d_{E_i} or d_{P_i} in solution at 23 °C and extrapolating the values toward the concentration c_{E_i} or $c_{P_i} = 0$. Activation volumes are extrapolated from the reaction temperature of 119.8–23 °C by using the Ely'anov equation.[23] According to the data listed in Table 4, the Diels–Alder dimerization leading to **16** shows an activation volume more negative and a ratio $\Delta V_0^*/\Delta V_R$ larger than those for the formation of *trans*-1,2-divinylcyclobutane (**17**) or 1,5-cyclooctadiene (**18**). These findings suggest a pericyclic Diels–Alder reaction competing with stepwise [2 + 2] or [4 + 4] cycloadditions.[24]

This interpretation of the pressure effect is strongly supported by a new stereochemical analysis of the dimerization of (*Z,Z*)-1,4-dideuterio-1,3-butadiene (**13**-1,4-D^Z) employing 400-MHz ^{1}H-NMR spectroscopy as an analytical tool, which was not available in 1975 when Stephenson et al.[21] reported their study. The dimerization of **13**-1,4-D^Z was carried out under various conditions described in Tables 5 and 10. The [4 + 2] and [2 + 2] cyclodimers **16**-D and **17**-D as well as recovered starting material **13**-D^Z were isolated by preparative GC. In recovered **13**-D^Z, the deuterium distribution analyzed from the ratio of the ^{1}H-NMR signals at = 5.21 and 6.34 assigned to 1,4-H^Z and 1,4-H^E, respectively, remained unchanged.

---

(17) Doering, W. von E.; Franck-Neumann, M.; Hasselmann, D.; Kaye, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 3833–3844. Berson, J. A.; Dervan, P. D. *J. Am. Chem. Soc.* **1973**, *95*, 267–269. Benson, S. W. *J. Chem. Phys.* **1967**, *46*, 4920–4926.

(18) (a) Doering, W. von E.; Roth, W. R.; Bauer, F.; Boenke, M.; Breuckmann, R.; Ruhkamp, J.; Wortmann, O. *Chem. Ber.* **1991**, *124*, 1461–1470. (b) Roth, W. R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499–2521.

(19) Doering, W. von E.; Belfield, K. D.; He, J. *J. Am. Chem. Soc.* **1993**, *115*, 5414–5421.

(20) Li, Y.; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478–7485.

(21) Stephenson, L. M.; Gemmer, R. V.; Current, S. P. *J. Am. Chem. Soc.* **1975**, *97*, 5909–5910; *J. Org. Chem.* **1977**, *42*, 212–214.

(22) Berson, J. A.; Malherbe, R. *J. Am. Chem. Soc.* **1975**, *97*, 5910–5912.

(23) (a) From the temperature dependence of molar volumes, Ely'anov et al.[23b] extrapolated a general constant $k_0 = (4.43 \pm 0.5) \times 10^{-3}$ K^{-1} to describe the temperature dependence of activation and reaction volumes. From the temperature dependence of the partial molar volumes of **16**, **17**, and **18**, the k_0 value for the volume of reaction of *trans*-1,2-divinylcyclobutane (**17**) to 4-vinylcyclohexene (**16**) or to 1,5-cyclooctadiene (**18**) can be derived to be $(2.526 \pm 0.039) \times 10^3$ and $(3.829 \pm 0.028) \times 10^{-3}$ K^{-1}, respectively.[29b] These values are on same order of magnitude with that given by El'yanov et al.[23b] (b) El'yanov, B. S.; Gonikberg, E. M. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 172–191. El'yanov, B.S.; Vasylvitskaya, E. M. *Rev. Phys. Chem. Jpn.* **1980**, *50*, 169–184.

(24) The surprisingly small activation volume found for the formation of the very minor product **18** seems to be inconsistent with a stepwise mechanism. The experimental error in the determination of the pressure dependence of its formation, however, is certainly larger than that given by the standard deviation (95% confidence). We speculate that the small ratio $\Delta V^*{}_0/\Delta V_R$ may indicate that **18** is formed via a stepwise [4 + 4] cycloaddition passing through the diradical intermediate (*Z,Z*)-**19**.

Table 4. Pressure Dependence of the Dimerization of Butadiene **13** (c_0 = 1.330 M, 0.997 M, and 0.665 M in *n*-Decane) at 119.8 °C

p (bar)	*t* (h)	## IVa ##	## IVb ##	## IVc ##	$\Sigma k \times 10^6$ (L mol^{-1} s^{-1})
600	18	93.2 ± 0.4	5.5 ± 0.4	1.3 ± 0.1	1.96 ± 0.04
740	23	94.0 ± 0.3	4.9 ± 0.4	1.2 ± 0.1	2.24 ± 0.10
960	18	94.9 ± 0.1	3.9 ± 0.2	1.2 ± 0.1	3.21 ± 0.27
1070	21	95.0 ± 0.3	3.8 ± 0.2	1.2 ± 0.1	3.62 ± 0.27
1150	15	95.2 ± 0.1	3.6 ± 0.1	1.2 ± 0.1	4.02 ± 0.16
1380	15	95.7 ± 0.1	3.2 ± 0.1	1.1 ± 0.1	5.28 ± 0.14
2020	16	96.1 ± 0.1	2.8 ± 0.1	1.1 ± 0.1	7.99 ± 0.48
2680	17	96.7 ± 0.1	2.3 ± 0.1	1.0 ± 0.1	13.6 ± 0.03
3440	13	97.1 ± 0.1	2.0 ± 0.1	0.9 ± 0.1	22.8 ± 1.21
3930	5	97.7 ± 0.1	1.7 ± 0.1	0.6 ± 0.1	29.4 ± 0.83
4350	6	97.5 ± 0.1	1.8 ± 0.1	0.7 ± 0.1	37.7 ± 0.08
5300	7	97.9 ± 0.1	1.5 ± 0.1	0.6 ± 0.1	58.1 ± 0.10
119 °C	$\Delta V_0^{\neq a}$	−(38.4 ± 0.6)	−(20.9 ± 0.4)	−(34.0 ± 0.9)	−(37.8 ± 0.6)
23 °C	$\Delta V_0^{\neq a}$	−26.5	−14.4	−23.5	
	$\Delta V_R{}^a$	−33.5	−24.4	−43.5	
	$\Delta V_0^{\neq}/\Delta V_R$	0.79	0.59	0.54	

[a] (cm^3/mol).

Table 5. Stereochemistry of the Thermal Dimerization of (*Z*,*Z*)-1,4-Dideuterio-1,3-butadiene (**13**-1,4-D^Z) (in *n*-Decane) to the Tetradeuterio-4-vinylcyclohexenes **16a–d**

run	*cis*:*trans* [**16a** + **16c**]:[**16b** + **16d**]	de^a	[**16a** + **16d**]:[**16b** + **16c**]	de^a
1a, 1 bar, 138 °C, 55 h	0.969:0.031^b	0.938	0.555:0.445^b	0.110
	0.971:0.029^c	0.942	0.561:0.439^c	0.122
1b, 8 kbar, 120 °C, 55 h	0.992:0.008^b	0.984	0.696:0.304^b	0.392
	0.996:0.004^c	0.992	0.712:0.288^c	0.424
2a, 1 bar, 120 °C, 48 h	0.967:0.033^b	0.934	0.599:0.401^b	0.198
	0.968:0.032^c	0.936	0.604:0.396^c	0.208
2b, 6.8 kbar, 120 °C, 48 h	>0.999:<0.001^b	>0.998	0.722:0.278^b	0.444
	0.996:0.004^c	0.992	0.733:0.267^c	0.466

[a] Diastereomeric excess. [b] ^{1}H-NMR in CDCl$_3$. [c] ^{1}H-NMR in C$_6$D$_6$.

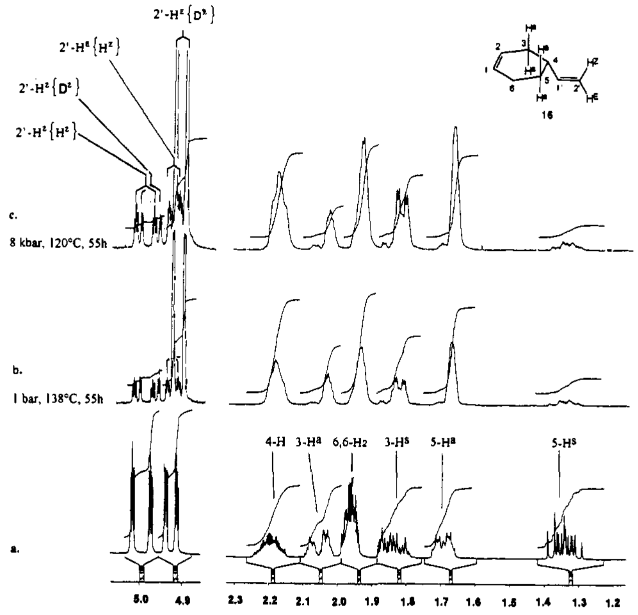


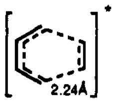
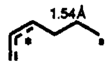
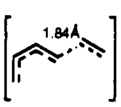
Figure 4. ^{1}H-NMR spectra (400 MHz, CDCl$_3$) of (a) **16**, (b) **16**-D from the thermolysis of **13**-1,4-D^Z at 138 °C, 1 bar, 55 h (run 1a), and (c) from the thermolysis of **13**-1,4-D^Z at 120 °C, 8 kbar, 55 h (run 1b).

In the ^{1}H-NMR spectrum of the Diels–Alder adduct **16**-D, shown in Figure 4, the signals assigned to vinyl hydrogen atoms 2′-H^Z{H^E} and 2′-H^E{H^Z} of the undeuterated adduct due to the geminate couplings constant (^2J(2′-H^Z, 2′-H^E) = 1.6 Hz) are separated from the signals assigned to 2′-H^Z{D^E} and 2′-H^E{D^Z} of the deuterated adducts **16**-D^Z and **16**-D^E. With the reasonable assumption that the configuration of the vinyl group is retained during both the pericyclic and stepwise Diels-Alder reactions, the ratio of these signals can be used as an internal standard for the deuterium distribution in starting **13**-D. The spectrum of the hydrogen atoms H^s and H^a at C-3, -4, -5, and -6 of **16** is similar to that of the corresponding [4 + 2] dimer **4** of chloroprene (**1**). The assignment of these signals, shown in Figure 4, could be confirmed by homonuclear double resonance experiments. In order to obtain the intensities of these signals as accurately as possible, ^{1}H-NMR spectra of **16**-D were recorded in two solvents (CDCl$_3$ and C$_6$D$_6$) and the signals were integrated in the same manner as described above for the stereochemical analysis of the dimerization of chloroprene **1**-D.

The product ratios [**16a** + **16c**]:[**16b** + **16d**] and [**16a** + **16d**]:[**16b** + **16c**] listed in Table 5 can be derived from the ratios of the signal intensities I(5-H^a):I(5-H^s) and I(3-H^s):I(3-H^a), respectively, in relation to I(2′-H^E{D^Z}):I(2′-H^Z{D^E}):I(2′-H^E{H^Z}) (Table 10). Deuterium distribution in the [2 + 2] cyclodimer **17**-D, isolated from the thermolysis of **13**-1,4-D^Z at 138 °C and 1 bar (run 1a), was determined analogously. The ratio I(3,4-H^s):I(3,4-H^a) = 53:47 (again related to I(2′-H^E{D^Z}):I(2′-H^Z{D^E}):I(2′-H^E{H^Z})) demonstrates that [2 + 2] cyclodimerization occurs nonstereospecifically, as expected.

In the Diels–Alder dimerization, the ratio of [**16a** + **16c**] to [**16b** + **16d**] is a measure of the *cis*:*trans* stereoselectivity, whereas [**16a** + **16d**]:[**16b** + **16c**] measures the *endo*:*exo* selectivity provided that the formation of the *trans*-adducts **16b**,**d** is negligible. Both ratios are significantly pressure dependent. From the data in Table 5, the reaction occurs with *97% cis-stereoselectivity at ambient pressure (1 bar) and >99% stereospecificity at high pressure (6.8–8 kbar).* These findings provide good evidence for the stereospecific pericyclic Diels–Alder mechanism in competi-

Table 6. Comparison between Molar Volumes V, van der Waals Volumes V_w (cm^3/mol), and Packing Coefficients η for the Pericyclic and Stepwise Cycloaddition of Ethene to 1,3-Butadiene

compound	d(g/cm^3)	$V = M/d$	$V_w{}^d$	$\eta = V_w/V$
$H_2C{=}CH_2$		59.9^a	25.5	0.4257
$H_2C{=}CH{-}CH{=}CH_2$		83.2^a	44.8	0.5385
$H_2C{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$	0.6880	119.4	63.9	0.5354
$H_2C{=}CH{-}CH_2{-}CH{=}CH{-}CH_3$	0.7000	117.4	63.9	0.5443
$H_2C{=}CH{-}CH{=}CH{-}CH_2{-}CH_3$	0.7050	116.5	63.8	0.5475
	0.8102	101.4	59.1	0.5829
 (23)*		109.1^b	63.6	
 24		119.3^c	64.7	
 (25)*		120.4^c	65.3	

^{a} Calculated values with volume increments.[36] ^{b} Calculated values with the packing coefficient of cyclohexene ($\eta = 0.5829$). ^{c} Calculated values with the average of the packing coefficients determined for the three isomeric hexadienes ($\eta = 0.5424$). ^{d} For the calculation of van der Waals volumes, the following van der Waals radii were used: R_w(H) = 1.17 Å and R_w(C) = 1.80 Å.

tion with a small amount of the nonstereospecific stepwise reaction, which can be almost completely suppressed by high pressure, and confirm the conclusion drawn from the different activation volumes found for the [4 + 2] and [2 + 2] cyclodimerizations of 1,3-butadiene. From the pressure dependence of the product ratio [**16a** + **16d**]:[**16b** + **16c**], it can be extrapolated that the *endo*-Diels–Alder reaction shows a slightly more negative activation volume than the corresponding *exo* reaction ($\Delta\Delta V^{*} \approx -2.5$ cm^3/mol) although both reactions are evidently pericyclic.

Comparison between Volumes of Activation and Reaction and the Corresponding van der Waals Volumes. The question has to be addressed, why are the activation volumes of pericyclic reactions smaller (more negative) than those of the corresponding stepwise reactions? In the past one has assumed that the simultaneous formation of two new bonds in a pericyclic [4 + 2] cycloaddition leads to a larger contraction of volumes than the formation of one bond in the rate-determining transition state of the stepwise reaction. The interpretation presented here is limited by the scope of Eyring's transition-state theory where the activation volume, as mentioned above, is considered to be the reaction volume of a transition state[1] and does not incorporate dynamic effects related to pressure-induced changes of viscosity.[25] In order to uncover the effect of differences in bonding on the volume of transition states, we calculated the intrinsic volumes, the so-called van der Waals volumes, V_W, of ground and transition structures for the pericyclic and stepwise cycloadditions of ethene to 1,3-butadiene (the prototype of Diels–Alder reactions) by following the method of Nakahara et al.[26] (Table 6). The necessary structural parameters—bond lengths and bond angles—required for such a calculation have been determined by force-field or quantum mechanical methods, and van der Waals radii were derived from X-ray data.[27]

The ratio V_W/V defined as the packing coefficient η is found to be generally larger for cyclic compounds than for the corresponding acyclic ones. Table 6 contains η values for cyclohexene and the three isomeric hexadienes as an example. The van der Waals volume of the Diels–Alder reaction[2,26,28] ($\Delta V_W = 59.1 - (44.8 + 25.5) = -11.2$ cm^3/mol) can be calculated to be only roughly a quarter of the experimentally accessible volume of reaction ($\Delta V = 101.4 - (83.2 + 59.9) = -41.7$ cm^3/mol). Consequently a significant part of the observed ΔV results from the higher packing of the cyclic product (compared to the acyclic starting materials) rather than from the changes in bonding. The difference between the van der Waals volumes of activation calculated for the pericyclic reaction ($\Delta V_W{}^{*} = 63.6 - (44.8 + 25.5) = -6.7$ cm^3/mol) and the stepwise reaction ($\Delta V_W{}^{*} = 65.3 - (44.8 + 25.5) = -5.0$ cm^3/mol) is small and is inconsistent with the experimental data listed in Tables 1 and 4. The comparison between the van der Waals volumes of the hexenediyl **24** and the transition structure [**24**]* for its formation shows that the effect on volumes caused by the change of bond lengths is rather small. In order to explain the finding that the activation volume of a pericyclic reaction is significantly more negative than that of the corresponding stepwise process, one has to assume that the packing coefficient of the pericyclic transition state is similar to that of the cyclic product whereas the transition state of the stepwise process is acyclic and has, therefore, a smaller packing coefficient. The difference between the activation volumes, $\Delta\Delta V^{*}$, calculated by using the packing coefficients of cyclohexene and the average of the three hexadienes for the transition structures of the pericyclic and stepwise Diels–Alder reactions ($\Delta V^{*} = 109.1 - (59.9 + 83.2) = -34.0$ cm^3/mol and $120.4 - (59.9 + 83.2) = -22.7$ cm^3/mol), respectively, is -11 cm^3/mol. This value is in good accord with the experimental findings (Tables 1 and 4). Therefore, the analysis of activation volumes seems to provide important information whether the geometry of a transition state is cyclic or acyclic. The conclusions drawn from this simple analysis are strongly supported by a Monte Carlo simulation resulting from activation and reaction volumes of the Diels–Alder reaction of ethene and 1,3-butadiene and the dimerization of 1,3-butadiene.

---

(25) (a) Kowa, L. N.; Schwarzer, D.; Troe, J.; Schroeder, J. *J. Chem. Phys.* **1992**, *97*, 4827–4835. (b) Firestone, R. A.; Vitale, M. A. *J. Org. Chem.* **1981**, *46*, 2160–2164.

(26) Yonhimura, Y.; Osugi, J.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 680–683. Yonhimura, Y.; Osugi, J.; Nakahara, M. *J. Am. Chem. Soc.* **1983**, *105*, 5414–5418.

(27) The van der Waals volumes V_W can be calculated by the computer program MOLVOL: Artschwager-Perl, U. Cycloadditionen unter hohem Druck. Ph.D. Dissertation, Ruhr-Universität Bochum, 1989. This program uses the cartesian coordinates of a molecular structure resulting from a force-field or quantum mechanical calculation and can be obtained on request.

(28) Similar calculations of van der Waals volumes have been carried out: Firestone, R.A.; Smith, G. M. *Chem. Ber.* **1989**, *122*, 1089–1094.

Table 7. Results of the Simulation for the Diels–Alder Reaction of Ethene with 1,3-Butadiene (**13**)

component 1	component 2	κ_1[a]	$\tilde{p}$	V_m (cm^3/mol)	$\Delta V^{\ne}$[b] (cm^3/mol)
ethene		1.0000	0.03	87.4567	
		1.0000	0.05	73.0561	
		1.0000	0.10	59.5632	
ethene	**13**	0.9063	0.03	92.2306	
		0.9063	0.05	76.9481	
		0.9063	0.10	62.8004	
ethene	[**23**]*	0.8966	0.03	95.7942	–57.8
		0.8966	0.05	81.1131	–36.7
		0.8966	0.10	66.5024	**–27.0**
ethene	cyclohexene	0.8966	0.03	95.4573	–61.0
		0.8966	0.05	80.3319	–44.2
		0.8966	0.10	66.1236	**–30.7**

[a] Molar fraction of the major component. [b] Activation or reaction volume calculated by means of eq 5 and the V_m values listed here.

Table 8. Results of the Simulation for the Butadiene Dimerization with an Excess of Butadiene **13** as the Solvent[a]

component 1	component 2	κ_1[b]	$\tilde{p}$	V_m	ΔV_{calcd}	ΔV_{exptl}
13			0.03	130.2303		
(44.8)		1.000	0.05	111.3103		
			0.10	93.6273		
13[c]			0.03	138.2482	–52.7	
	[*endo*-**20**]*	0.8966	0.05	118.9595	–37.4	
	(81.2)		0.10	99.9150	**–32.8**	**–27.9**
13[c]			0.03	139.6009	–39.6	
	[*exo*-**20**]*	0.8966	0.05	119.5622	–31.5	
	(81.1)		0.10	100.1287	**–30.8**	**–25.4**
13			0.03	137.2723	–62.2	
	16	0.8966	0.05	119.1446	–35.6	
	(77.5)		0.10	99.6512	**–35.4**	**–33.5**
13			0.03	140.1404	–34.4	
	[(*E*,*E*)-**21**]*	0.8966	0.05	120.4285	–23.2	
	(83.2)		0.10	101.9174	**–13.5**	**–14.6**
13	(*E*,*E*)-**19**		0.03	138.7118	–48.2	
	(82.6)	0.8966	0.05	119.5724	–31.4	
			0.10	101.3813	**–18.7**	
13	*trans*-**17**		0.03	139.4278	–41.3	
	(79.3)	0.8966	0.05	119.4552	–32.6	
			0.10	100.2311	**–29.8**	**–24.2**
13	*cis*-**17**		0.03	138.4439	–50.8	
	(79.1)	0.8966	0.05	119.1691	–35.3	
			0.10	100.7404	**–24.9**	
13	**18**[d]		0.03	136.6255	–68.4	
	(76.9)	0.8966	0.05	118.0674	–46.0	
			0.10	99.2419	**–39.4**	**–43.5**
13	**18**[e]		0.03	136.8915	–65.8	
	(76.6)	0.8966	0.05	117.6423	–50.1	
			0.10	99.1259	**–40.5**	**–43.5**

[a] The van der Waals volumes of the single components V_w(cm^3/mol) are shown in parentheses. [b] Molar fraction of **13**: $N_S = 208$, $N_R = 24$, shown as a comparison between the calculated and experimental activation and reaction volumes ΔV_{calcd} and ΔV_{exptl}(cm^3/mol), respectively. [c] These calculations were performed with the double size of the ensemble. The values do not differ significantly from those obtained with the normal size. [d] Chair confirmation. [e] Twist-boat conformation.

The computational method and the results of the simulation are described in the Appendix.

Conclusion. The activation and reaction volumes simulated for the pericyclic Diels–Alder reaction of ethene with 1,3-butadiene (Table 7) are on the same order of magnitude ($\tilde{p} = 0.1$; $\Delta V^{\ne} = -27.0$ cm^3/mol, $\Delta V_R = -30.7$ cm^3/mol, $\Delta V^{\ne}/\Delta V_R = 0.88$), consistent with the experimental findings for many Diels–Alder reactions.[1]

The results for the simulated activation and reaction volumes of the butadiene dimerization are summarized in Table 8. Although the *endo*-Diels–Alder dimerization passing through the transition state [*endo*-20]* has the most negative activation volume, it is only slightly more negative than the corresponding *exo*-reaction passing through [*exo*-**20**]* ($\Delta\Delta V^{\ne}_{calcd} = \Delta V^{\ne}_{endo} - \Delta V^{\ne}_{exo} = -1.8$ cm^3/mol) and is, therefore, favored by high pressure.

The activation volume calculated for the stepwise [2 + 2] cyclodimerization passing through [(*E*,*E*)-**21**]* is substantially less negative than those calculated for the pericyclic Diels–Alder reactions mentioned above ($\Delta\Delta V^{\ne}_{calcd} = \Delta V^{\ne}_{endo} - \Delta V^{\ne}[2+2] = -18$ cm^3/mol). The calculations are, indeed, in surprisingly good agreement with the experimental data. The difference between the activation volumes found for the *endo*- and *exo*-Diels–Alder dimerizations is $\Delta\Delta V^{\ne}_{exptl} = -2.1$ cm^3/mol and that for the competing [2 + 2] and [4 + 2] cyclodimerizations is $\Delta\Delta V^{\ne}_{exptl} = \Delta V^{\ne}_{endo} - \Delta V^{\ne}[2+2] = -13.3$ cm^3/mol. A comparably good agreement between calculated and experimental data is also found for reaction volumes (Table 8). It must be noted that the van der Waals volumes of the transition structures of the various dimerization processes listed in Table 8 do not differ significantly from one another. The preference of Diels–Alder reactions over [2 + 2] cyclodimerizations is, therefore, a configurational effect which can be explained by the different packing of cyclic and acyclic states. In order to demonstrate the effect of solvent, we have started a simulation of the butadiene dimerization where the nonreacting butadiene molecules are replaced by spherical molecules like helium ($R_w = 1.20$ Å) or radon ($R_w = 3.00$ Å), both again modeled as hard spheres. The preliminary results of these simulations show that the difference between the activation volumes of the [4 + 2] and [2 + 2] cycloaddition becomes smaller, especially with helium as the solvent. This again corroborates our view that an interpretation of activation and reaction volumes cannot be based only on properties of single molecules only but requires consideration of configurational effects. It is surprising that the simple molecular model used here (rigid framework of fused hard spheres) is able to account for experimentally observed reaction and activation volumes almost quantitatively. At the highest pressure used in these simulations, some of the molar volumes or reaction and activation volumes show the tendency, however, to be still slightly too negative. We hope to obtain an even better agreement with the experimental data by incorporating an appropriate soft-interaction potential.

With this simple conception, that cyclic ground or transition states show larger packing coefficients than the corresponding acyclic states, one can now understand why pericyclic rearrangements like Cope rearrangements, electrocyclic reactions, or intramolecular Diels–Alder reactions are accelerated by high pressure, having substantially negative volumes of activation. In ref 29 it has been shown that the size of the volume of activation and reaction depends on the number and size of the rings newly formed.

Experimental Section

General Methods. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a Bruker AM 400 (^{1}H-NMR, 400 MHz; ^{13}C-NMR, 100.6 MHz) and a Bruker WP 80 (^{1}H-NMR, 80 MHz) instrument with tetramethylsilane as the internal standard (δ(TMS) = 0). GC analyses were performed on a Hewlett-Packard HP 5890 A (fid) with a HP 3390 integrator (carrier gas, N_2) and Siemens Sichromat 2 (FID) (carrier gas, He) using fused silica columns. Preparative GC separations were performed on a Varian Aerograph 90 P (WLD) (carrier gas, He).

(*E*)- and (*Z*)-1-Deuterio-2-chloro-1,3-butadiene (1-D^E + 1-D^Z).[14] A mixture of vinylacetylene (5.0 g, 96 mmol), ND_4Cl (1.1 g, 19 mmol), and

---

(29) (a) Diedrich, M. K.; Hochstrate, D.; Klärner, F.-G.; Zimny, B. *Angew. Chem.* **1994**, *106*, 1135–1137; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, in press. (b) Doering, W. V. E.; Birladeanu, L.; Sarma, K.; Teles, J. H.; Klärner, F.-G.; Gehrke, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 4289–4297.

(30) Press, W. H.; Flannery; B. P.; Teukolsky, S. P.; Vetterling, W. T. *Numerical Recipes*; Cambridge University Press: Cambridge, U.K., 1986.

(31) Deiters, U. K. *Mol. Simul.* **1989**, *3*, 343–344.

(32) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Clarendon Press: Oxford, 1987.

(33) Kolafa, J. *Mol. Phys.* **1988**, *63*, 599.

(34) Boublik, T. *Mol Phys.* **1981**, *42*, 209–216.

(35) Boublik, T.; Nezbeda, I. *Chem. Phys. Lett.* **1977**, *46*, 315–316.

Table 9. Pressure Dependence of the Rate Constants $k \times 10^7$ (L mol^{-1} s^{-1}) in the Dimerization of 1,3-Butadiene (**13**) at 119.8 °C Calculated from the Overall Rate Constants $\sum k$ and the Product Ratio Listed in Table 4

p (bar)	600	740	960	1070	1150	1380	2020	2680	3440	3930	4350	5300
k(2**13** → **16**)	18.3	21.0	30.5	34.4	38.3	50.6	76.8	130	221	287	368	569
k(2**13** → **17**)	1.08	1.09	1.24	1.36	1.45	1.67	2.20	3.07	4.57	5.09	6.90	8.37
k(2**13** → **18**)	0.261	0.275	0.385	0.432	0.486	0.608	0.879	1.43	2.07	1.88	2.64	3.66

CuCl (2.5 g, 25 mmol) dissolved in saturated DCl–D$_2$O (17.9 g) was stirred in a sealed pressure flask for 4 h at 30 °C. The organic and aqueous layers were separated, and the organic layer was dried over Na$_2$SO$_4$. Bulb to bulb distillation (25 °C, 0.1 mmHg) and purification by preparative GC (4-m $^1/_4$-in. column packed with 20% DEGS on chromosorp P, 100 °C) gave 4.5 g (53% yield) of a mixture containing **1**-D^E, **1**-D^Z, and **1** in a 48.9:48.5:2.6 ratio determined by the ^{1}H-NMR spectrum (400 MHz, CDCl$_3$): δ 5.32 (dm, 4-H$^{\mathrm{E}}$, ^3J(3-H, 4-H^E) = 10.5 Hz), 5.36 (m, 1-H^E{D^Z}, 5.38 (m, 1-H^E{H^Z}), 5.40 (m, 1-H^Z{D^E}), 5.41 (m, 1-H^Z{H^E}),5.64 (dm, 4-H^Z, ^3J(3-H, 4-H^2) = 17.0 Hz), 6.41 (ddd, 3-H).

(*E*)-1-Deuterio-2-chloro-1,3-butadiene (1-D^E).[15] (a) A solution of bromine (268.5 g, 1.68 mol) in 150 mL of CHCl$_3$ was dropped to a stirred solution of chloroprene (**1**) (150 g, 1.7 mol) in 800 mL of CHCl$_3$ at 0 °C. After 1 h the cooling bath was removed. The reaction mixture was allowed to warm to room temperature and concentrated in vacuo. Bulb to bulb distillation afforded 1,4-dibromo-2-chloro-2-butene (385 g, 92% yield, bp 54 °C at 0.1 mmHg). ^{1}H-NMR (80 MHz, CDCl$_3$): δ 4.02 (d, 2*H*, 4-H, ^3J(2-H, 3-H) = 8.0 Hz), 4.10 (s, 2*H*, 1-H), 6.20 (t, 1*H*, 3-H).

(b) 1,4-Dibromo-2-chloro-2-butene (190 g, 0.77 mol) was slowly added to a stirred solution of KOH (112 g, 2 mol) in 1 L of ethanol (96%) at 0 °C. After stirring of the reaction mixture at room temperature for 14 h, the precipitated KBr was removed by suction filtration. The filtrate was diluted by water in the ratio of 1:1 and extracted three times by pentane. The pentane extract was dried over MgSO$_4$ and concentrated in vacuo. The concentrate containing ca. 60% of **14** and ca 40% of four isomeric bromochlorobutadienes was separated by vacuum distillation into two fractions. The first fraction consisted of **1**-Br^Z, **1**-Br^E, and two unknown isomers (46 g, 36% yield, bp 64 °C at 10 mmHg) in a ratio of 78.7:3.8:9.3:8.2, analyzed by GC (25 m, silicon oil OV 17, 80 °C), and the second fraction consisted of **14** (63 g, 46% yield, bp 101 °C at 10 mmHg). Preparative GC separation of the first fraction (25 g, 2-m $^1/_4$-in. column packed with 20% silicon oil XE 60 on chromosorp P at 105 °C) afforded **1**-Br^Z (7.5 g, 98% GC purity) and **1**-Br^E (ca. 0.5 g, 92% GC purity) as fractions 2 and 4. ^{1}H-NMR (80 MHz, CDCl$_3$) of **1**-Br^Z: δ 5.53 (dm, 1*H*, 4-H^E, ^{3}J(3-H, 4-H^E) = 10.0 Hz), 5.87 (dm, 1*H*, 4-H^Z, ^3J(3-H, 4-H^Z) = 16.5 Hz), 6.45 (d, 1*H*, 1-H^E, ^4J(1-H, 3-H) ≈ 1 Hz), 6.93 (ddd, 1*H*, 3-H). ^{1}H NMR of **1**-Br^E: δ 5.34 (dm, 1*H*, 4-H^E, ^3J(3-H, 4-H^E) = 10.5 Hz, ^2J(4-H^Z, 4-H^E) = 1.0 Hz), 5.70 (dm, 1*H*, 4-H^Z, ^3J(3-H, 4-H^Z) = 16.5 Hz), 6.42 (dd, 1*H*, 3-H), 6.63 (s, 1*H*, 1-H^Z). The structural assignments of **1**-Br^Z and **1**-Br^E rely on the different chemical shifts of 1-H^E and 1-H^Z. 1-H^E absorbs at a lower δ value than 1-H^Z, consistent with the corresponding hydrogen atoms in vinylchloride (δ-(2-H^E) 5.38, (2-H^Z) 5.43). ^{1}H NMR of **14**: 1.17, 1.19 (t, 6*H*, 2 × CH$_3$, $_3J$(CH$_2$CH$_3$) = 7.0 Hz), 3.46, 3.48 (q, 4*H*, 2 × CH$_2$), 4.00 (dd, 2*H*, 1-H, ^4J(1-H, 3-H) ≈ 1 Hz), 4.14 (ddd, 2*H*, 4-H, ^3J(3-H, 4-H) = 5.5 Hz), 5.94 (tdd, 1*H*, 3-H).

(c) **1**-Br^Z (3.16 g, 18.9 mmol) was added to a vigorously stirred mixture of LiAlD$_4$ (1.0 g, 23.9 mmol, degree of deuteration ≤ 99.5%) and 25 mL of dry ether under argon at 0 °C in portions over a period of 10 min. The reaction mixture was stirred at 0 °C for 48 h. After bulb to bulb distillation (25 °C, 0.05 mmHg) to remove the nonvolatile compounds (unconverted LiAlD$_4$ and LiBr or LiCl), the solution was concentrated at ambient pressure. Purification by preparative GC (2-m $^1/_4$-in. column packed with 20% silicon oil DC 200 on chromosorp P, 60 °C) afforded a mixture of **1**-D^E, **1**-D^Z, and **1** (67 mg, 4% yield) in the ratio 94.2:2.2:3.6 determined by ^{1}H-NMR (Figure 1c).

Thermal Dimerization of 1 and 1-D^E. (a) A solution of dry **1** (5.0 g, 56.5 mmol) and bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide (BHMPS, 25 mg) in 5 mL of dry toluene was heated in a sealed pyrex tube under argon at 50 °C for 16 h. The product ratio listed in Table 2 was analyzed by GC (39 m, silicon oil OV 101, 100 °C, retention times (min) of 9.0 (**5**), 11.7 (**4**), 12.9 (**3**), 13.1 (**2**), and 18.8 (1,6-dichlorocycloocta-1,5-diene)). The products were separated by preparative GC (2-m $^1/_4$-in. column packed with 20% silicon oil SE 30 on chromosorp P, 70 °C, retention times (min) of 11.0 (**5**), 18.5 (**4**), 23.5 (**2** + **3**), and 40 (1,6-dichlorocycloocta-1,5-diene)), and separation of **2** and **3** was feasible with a 4-m $^1/_4$-in. column packed 20% reoplex on chromosorp P (140 °C, retention times (min) of 29.8 (**3**) and 31.5 (**2**)). The desired products **4** and **5** were obtained in 95.5 and 95.3% GC purity, respectively. The spectra agree with the literature data. ^{1}H-NMR (400 MHz, CDCl$_3$) of **4** (Figure 2a): 2.01 (m, 1*H*, 5-H^s, ^2J(5-H^s, 5-H^a) = 14.0 Hz), 2.17 (m, 1*H*, 5-H^a), 2.36 (m, 1*H*, 6-H^s, ^2J(6-H^s, 6-H^a) = 17.0 Hz), 2.61 (m, 2*H*, 3-H^s, 3-H^a), 2.67 (m, 1*H*, 6-H^a), 5.16 (d, 1*H*, 2′-H^E, ^3J(1′-H, 2′-H^E) = 10.8 Hz), 5.29 (d, 1H, 2′-H^Z, ^3J(1′-H, 2′-H^Z) = 17.2 Hz), 5.72 (m, 1*H*, 2-H), 6.04 (dd, 1*H*, 1′-H). ^{1}H NMR of **5**: 2.32, 2.77 (AA′BB′ spectrum, 3-, 4-H^A, 3-, 4-H^B), 5.33 (dd, 2*H*, 2′-H^E, ^3J(1′-H, 2′-H^E) = 10.6 Hz), 5.43 (dd, 2*H*, 2′-H^Z, ^{3}J(1′-H, 2′-H^Z) = 17.0 Hz, ^2J(2′-H^Z, 2′-H^E) = 0.7 Hz), 6.24 (dd, 2*H*, 1′-H).

(b) The solution of the mixture of **1**-D^E, **1**-D^Z, and **1** (67 mg, 94.2:2.2:3.6) and BHMPS (1 mg) in toluene (67 mg) was heated in a sealed pyrex tube under argon at 50 °C for 30 h. The GC analysis and separation were performed as described for the thermolysis of **1**. The deuterium distributions in recovered 1-D^E, 1-D^Z, and **1** (Figure 1d, Scheme 1) and in the products **4**-D and **5**-D were determined by ^{1}H-NMR (400 MHz, CDCl$_3$). **4**-D (Figure 2b): δ 2.01 (m, I(5-H^s) = 0.386 ± 0.03), 2.17 (m, I(5-H^a) = 0.550 ± 0.03), 2.36 (m, I(6-H^s) = 0.580 ± 0.03), 2.61, 2.67 (m, I(3-H$_2$ + 6-H^a) = 2.289 ± 0.120). The intensities I are related to the average of I(2-H), I(1′-H), I(2′-H^Z), and I(2′-H^E): $I_{\mathrm{ave}} \equiv 1.000$. **5**-D: δ 2.32 (d, I(3-H^A{4-H^B}) ≈ 0.48, $^3J_{AB}$ = 9 Hz), 2.32 (s, I(3-, 4-H^A)/2 ≈ 0.34), 2.77 (d, I(4-H^B{3-H^A}) ≈ 0.48), 2.77 (s, I(3-, 4-H^B)/2 ≈ 0.18).

Pressure Dependence of the Dimerization of 1,3-Butadiene (13) (a) Measurement of the Butadiene Concentration, [13]. Gaseous **13** was condensed into degassed dry *n*-decane (100 mL, distilled over LiAlH$_4$) at –78 °C for 0.5 h. The stirred mixture was warmed to 30 °C for 3 h to obtain a saturated solution of **13** in *n*-decane. 1,4-Dioxane (150 μL, 152.67 mg) was added to the solution of **13** in *n*-decane (1.85 mL). (We examined independently that the mixture between 1,4-dioxane, *n*-nonane, and *n*-decane does not show a contraction of volume.) The molar concentration of 1,4-dioxane can be calculated to be [1,4-dioxane] = 152.67/2(88.11) = 0.8664 M. In the ^{1}H-NMR spectrum (80 MHz, CDCl$_3$), the intensities of signals at δ 3.71 (s, 8*H*, 1,4-dioxane), 5.20, and 6.35 (m, 6*H*, **13**) were measured to be I(8*H*, 1,4-dioxane):I(6*H*, **13**) = 9.15:10.15. From these data, the desired concentration of **13** can be calculated to be [**13**] = 0.8664(10.15/9.15)(8/6)(2.00/1.85) = 1.3854 M. *n*-Nonane (1.0 mL, 711.34 mg) (as the internal GC standard) and bis(3-*tert*-butyl-4-hydroxy-5-methylphenyl) sulfide (BHMPS) (97.49 mg) (as the inhibitor of radical-chain polymerization of **13**) were added to the solution of **13** in *n*-decane (24.0 mL). Parts of this solution ([**13**] = 1.330 M) were diluted by *n*-decane to obtain the concentrations given in Table 4. The GC area factor between 4-vinylcyclohexene (**16**) and *n*-nonane was measured with a solution of **16** (80.92 mg) and *n*-nonane (70.92 mg) in toluene. The GC area factors among the isomeric dimers **16**, **17**, and **18** were assumed to be f = 1.000.

(b) Kinetic Analysis (Determination of Activation Volumes). Portions (0.2 mL) of the three solutions of **13** ([**13**]$_0$ = 1.330 M, 0.997 M, and 0.665 M), *n*-nonane (c = 28.45 mg/mL, 21.34 mg/mL, and 14.23 mg/mL), and catalytic amounts of BHMPS) in *n*-decane were sealed in PTFE tubes (pretreated with refluxing Et$_3$N in order to avoid acid catalysis at the surface of PTFE tubes), placed in a 7-kbar autoclave, and heated at different pressures as stated in Table 4. In each run, three separated samples containing the three different concentrations of **13** were heated under the same conditions. The degree of conversion (formation of **16**, **17**, and **18** relative to the internal standard *n*-nonane [**16** + **17** + **18**]$_t$ and the product ratio [**16**:**17**:**18**]$_t$) was analyzed by GC (39 m, silicon oil OV 101, 70 °C, retention times (min) of 5.2 (**13**), 6.4 (**17**), 6.9 (**16**), 7.9 (*n*-nonane), 8.5 (**18**), and 11.8 (*n*-decane)). The pressure-dependent overall rate constant $\sum k$ was calculated from the formation of [**16** + **17** + **18**]$_t$ according to the second-order rate law: $\sum k = (1/t)[(1/[\mathbf{13}]_t) - (1/[\mathbf{13}]_0)]$; $[\mathbf{13}]_t = [\mathbf{13}]_0 - [\mathbf{16} + \mathbf{17} + \mathbf{18}]_t$. The rate constants $\sum k$ shown in Table 4 are the average of the values calculated from the three samples starting with a different concentration [**13**]$_0$ in each run. From the rate constants $\sum k$ and the product ratios listed in Table 4, the individual rate constants k(**16**), k(**17**), and k(**18**) for the formation of **16**, **17**, and **18** were calculated (Table 9). The activation volumes ΔV^{*}_0 at 119 °C included in Table 4 were derived from the nonlinear correlation $\ln(k)_p$

Table 10. ^{1}H-NMR Analysis (400 MHz, $CDCl_3$ or C_6D_6) of the Thermal Dimerization of (*Z,Z*)-1,4-Dideuterio-1,3-butadiene (**13**-1,4-D^Z)[a]

			run 1a		run 1b		run 2a		run 2b	
	δ (ppm)[c]	δ (ppm)[d]	I[c]	I[d]	I[c]	I[d]	I[c]	I[d]	I[c]	I[d]
1,2-H_2	5.65	5.63	2.02	1.93	1.98	1.96	2.04	1.96	2.00	2.04
3-H^s	1.82	1.80	0.597	0.612	0.727	0.734	0.635	0.634	0.710	0.730
3-H^a	2.07	2.02	0.509	0.510	0.392	0.376	0.487	0.461	0.337	0.342
4-H	2.23	2.16	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
5-H^s	1.36	1.30	0.182	0.160	0.138	0.137	0.152	0.165	0.108	0.121
5-H^a	1.73	1.66	0.942	0.926	0.959	0.975	0.964	0.983	0.976	0.986
6-H_2	2.03	1.93	1.08	1.08	1.07	1.09	1.11	1.10	1.05	1.09
1′-H	5.81	5.75	1.01	0.95	0.99	0.96	1.03	0.98	0.94	1.00
2′-$H^Z\{H^E\}$	4.99	4.98	0.083	0.069	0.072	0.073	0.085	0.088	0.079	0.087
2′-$H^Z\{D^E\}$	4.98	4.97	0.071	0.057	0.055	0.051	0.037	0.038	0.024	0.031
2′-$H^E\{H^Z\}$[e]	4.92	4.93	0.083	0.096	0.072	0.073	0.085	0.088	0.079	0.087
2′-$H^E\{D^Z\}$[e]	4.91	4.92	0.871	0.808	0.856	0.837	0.897	0.842	0.857	0.900

[a] Run 1: **13**-1,4-D^Z (25% in *n*-decane, $I(1\text{-}H^E):I(1\text{-}H^Z) = 89.0:11.0$). (a) 55 h at 138 °C, 1 bar, 70% conversion, product ratio[b] of [**16**-D]:[**17**-D]:[**18**-D] = 93.8:4.2:2.0. (b) 55 h at 120 °C, 8 kbar, >99% conversion, product ratio[b] of [**16**-D]:[**17**-D]:[**18**-D] = 99.2:0.4:0.3. Run 2: **13**-1,4-D^Z 10% in *n*-decane, $I(1\text{-}H^E):I(1\text{-}H^Z) = 90.7:9.3$. (a) 48 h at 120 °C, 1 bar, 40% conversion, product ratio[b] of [**16**-D]:[**17**-D]:[**18**-D] = 93.6:4.9:1.4. Recovered **13**-1,4-D^Z ($I(1\text{-}H^E):I(1\text{-}H^Z) = 90.4:9.6$). (b) 48 h at 120 °C, 6.8 kbar, 80% conversion, product ratio[b] of [**16**-D]:[**17**-D]:[**18**-D] = 98.4:0.6:1.0. Recovered **13**-1,4-D^Z ($I(1\text{-}H^E):I(1\text{-}H^Z) = 90.3:9.7$). [b] Determined by GC. [c] In $CDCl_3$. [d] In C_6D_6. [e] Due to the partial overlap, the signals assigned to 2′-$H^E\{H^Z\}$ and 2′-$H^E\{D^Z\}$ cannot be integrated separately. Their intensities are determined by subtracting the intensity $I(2'\text{-}H^Z\{H^E\})$ from the total integral $I(2'\text{-}H^E\{H^Z\}+2'\text{-}H^E\{D^Z\})$.

$= a + bp + cp^2$, $\Delta V^{*}_0 = -bRT$ ($R = 83.14$ cm^3 bar K^{-1} mol^{-1}). For a comparison with the reaction volumes, the activation volumes $\Delta V^{*}_0(T)$ determined at 119 °C are extrapolated to $T_0 = 23$ °C using the El'yanov equation: $\Delta V^{*}_0(T_o) = \Delta V^{*}_0(T)/[1 + (0.004\ 43)(T - T_0)]$.[23]

(c) Determination of Reaction Volumes. The partial molar volumes V of **16**, **17**, and **18** were determined from the densities d of solution measured for various concentrations c in *n*-decane at 23 °C (room temperature) by using the equation $\Phi = (M/d_0) - [(1000/c)(d - d_0)/d_0]$ (M, molecular weight; d_0, density of the pure solvent) and the linear extrapolation of Φ vs $c \rightarrow 0$: $V(\mathbf{16}) = 132.9$ (130.8 in *n*-heptane), $V(\mathbf{17}) = 142.0$ (140.6 in *n*-heptane), and $V(\mathbf{18}) = 123.4$ (122.9 in *n*-heptane) (cm^3/mol). Molar volumes can be calculated by group increments (with corrections for the nearest neighbors) published by Exner.[36] The values calculated for 1,3-butadiene (**13**) and 4-vinylcyclohexene (**16**) ($V(\mathbf{13}) = 83.2$[37] and $V(\mathbf{16}) = 131.6$ cm^3/mol) are in good agreement with those obtained from the density measurement. From the experimental data $V(\mathbf{17})$ and $V(\mathbf{18})$, increments for the hitherto unknown special structural correction terms[36] for the closure of a cyclobutane and 1,5-cyclooctadiene ring can be calculated to be I(cyclobutane) = 22.9 or 21.5 cm^3/mol and I(1,5-cyclooctadiene) = 5.0 or 4.5 cm^3/mol. The volume of reaction for the dimerization of butadiene listed in Table 4 is calculated with the equation $\Delta V_R = V(\text{dimer}) - 2V(\mathbf{13})$.

(*Z,Z*)-1,4-Dideuterio-1,3-butadiene (13-1,4-D_2). A mixture (*Z.Z*)-, (*Z,E*)-, and (*E,E*)-1,4-dichloro-1,3-butadiene in a 29.9:50.2:19.9 ratio determined by GC (40 m, silicon oil OV 17, 50 °C) was prepared according to the procedure published by P. D. Bartlett and G. E. H. Wallbillich and modified by M. Christl and G. Müller.[38] On a small scale, the diastereomers were separated by preparative GC (2-m $^1/_4$-in. column packed with 20% apiezone on chromosorp P) as described by Bartlett and Wallbillich.[38] On a larger scale in quantities of 20 g, (*Z.Z*)-1,4-dichloro-1,3-butadiene could be separated from the mixture of the (*Z,E*)- and (*E.E*)-isomers by separated fractional distillation using a "30-cm Fischer Spaltrohrsystem", bp 58–62 °C (bath temperature, 81.5 ± 0.5 °C; pressure, 84.0 ± 0.5 mmHg). The first distillate contained the (*Z.Z*)-, (*Z.E*)-, and (*E.E*)-isomes in a 87.7:10.2:2.1 ratio (the residue, 3.7:68.6:27.6), and the second distillate, in a 98.2:1.6:0.2 ratio (the residue, 16.4:66.3:17.4). ^{1}H-NMR (400 MHz, $CDCl_3$) of (*Z.Z*)-1,4-dichloro-1,3-butadiene: 6.22, 6.73 (AA′XX′ spectrum, ^3J(1-H, 2-H) = 7.1 Hz, ^4J(1-H, 3-H) = –0.8 Hz, ^5J(1-H, 4-H) = 1.0 Hz, ^3J(2-H, 3-H) = 9.5 Hz). ^{1}H NMR of (*Z.E*)-1,4-dichloro-1,3-butadiene: δ 6.02 (ddd, 1*H*, 1-H, ^3J(1-H, 2-H) = 7.3 Hz, ^4J(1-H, 3-H) ≈ 1 Hz; ^5J(1-H, 4-H) ≈ 1 Hz), 6.24 (ddd, 1*H*, 2-H, ^3J(2-H, 3-H) = 11.0 Hz, ^4J(2-H, 4-H) ≈ 1 Hz), 6.37 (ddd, 1*H*, 4-H, ^3J(3-H, 4-H) = 13.5 Hz), 6.87 (ddd, 1*H*, 3-H). ^{1}H NMR of (*E,E*)-1,4-dichloro-1,3-butadiene: δ 6.24, 6.78 (AA′XX′ spectrum, ^3J(1-H, 2-H) = 13.4 Hz, ^4J(1-H, 3-H) = 0.7 Hz, ^5J(1-H, 4-H) = –0.7 Hz, ^{3}J (2-H, 3-H) = 11.0 Hz).

(*Z.Z*)-1,4-Dideuterio-1,3-butadiene (**13**-1,4-D^Z) was prepared from pure (*Z.Z*)-1,4-dichloro-1,3-butadiene via Zu–Cn couple reduction according to the procedure reported by L. M. Stephenson, R. V. Gemmer, and S. P. Current.[21] The intensities of the signals at δ 5.07, 5.20, and 6.33 assigned to 1-H^E, 1-H^Z, and 2-H listed in Table 10 were determined in the various ^{1}H-NMR spectra of **13**-D (runs 1 and 2).

Thermal Dimerization of 13-1,4-D^Z. The solution of **13**-1,4-D^Z (25%) and BHMPS (catalytic amounts) in *n*-decane (6 mL) degassed under Ar was heated either in a sealed 10-mL pyrex ampule at 138 °C, 1 bar for 55 h (Table 10, run 1a), or in a sealed PTFE tube (pretreated with refluxing Et_3N) placed in a 10-kbar autoclave at 120 °C, 8 kbar for 55 h (Table 10, run 1b). These experiments were repeated with a solution of **13**-1,4-D^Z (10%) in *n*-decane at 120 °C, 1 bar for 48 h, and 120 °C, 6.8 kbar for 48 h (Table 10, run 2a,b). After each thermolysis, the product ratio and the conversion of **13**-1,4-D^Z listed in Table 10 were determined by GC (the product ratio as described for the thermolysis of **13** and the conversion by comparison of the GC peaks of butadiene and *n*-decane before and after the thermolysis). From the thermolysis of run 1a, **16**-D and **17**-D were separated by preparative GC (2-m $^1/_4$-in. column packed with 20% silicon oil DC 550 on chromosorp P, 102 °C, retention times (min) of 0.8 (**13**-1,4-D^Z), 3.5 (**17**-D), and 7.8 (**16**-D)), and from all the other reactions (runs 1b and 2a,b), only **16**-D was separated by GC. In the case of run 2a,b, unconverted **13**-D was recovered by distillation prior to the GC separation and analyzed by ^{1}H-NMR (400 MHz, $CDCl_3$). The results of the deuterium distribution in isolated **16**-D (99% purity, GC) obtained from the ^{1}H-NMR spectra shown in Figure 4 are summarized in Tables 5 and 11.

$I(2'\text{-}H^E\{D^Z\}) \triangleq a$; $I(2'\text{-}H^Z\{D^E\}) \triangleq b$; $I(2'\text{-}H^E\{H^Z\}) = I(2'\text{-}H^Z\{H^E\}) \triangleq c$; [**16a** + **16c**] $\triangleq x$; [**16b** + **16d**] $\triangleq y$; $I(5\text{-}H^s):I(5\text{-}H^a) = d$. The intensities of the signals a, b, and c can be calculated from the ratio $a:b:c$ and the sum $a + b + c = 1$. The ratio $x:y$ listed in Table 5 can be derived from the relations $d = (ax + by + c)/(ay + bx + c)$ and $x + y = 1$. The same procedure was used to calculate the ratio [**16a** + **16d**]:[**16b** + **16c**]. ^{1}H-NMR (400 MHz, $CDCl_3$) of **17**-D: 1.72 (m, $I(3\text{-}, 4\text{-}H^s) = 0.96$), 1.93 (m, $I(3\text{-}, 4\text{-}H^a) = 1.18$), 2.66 (m, $I(1\text{-}, 2\text{-}H) \equiv 2.00$), 4.88 (m, $I(2'\text{-}H^E\{D^Z\} + (2'\text{-}H^E\{H^Z\})/2) \approx 1.8$ $^3J(1'\text{-}H, 2'\text{-}H^Z) = 16.2$ Hz, $^2J(2'\text{-}H^Z, 2'\text{-}H^E) \approx 1.6$ Hz, $^4J(1\text{-}H, 2'\text{-}H^E) \approx 0.2$ Hz), 4.94 (m, $I(2'\text{-}H^E\{H^Z\} + 2'\text{-}H^Z\{D^E\})/2 \approx 0.2$), 4.95 (ddd, $I(2'\text{-}H^Z\{H^E\}) = 0.16$, $^3J(1'\text{-}H, 2'\text{-}H^E) = 10.4$ Hz, $^4J(1\text{-}H, 2'\text{-}H^Z) \approx 1.2$ Hz), 4.96 (d, $I(2'\text{-}H^Z\{D^E\})/2 \approx 0.1$), 5.86 (m, $I(1'\text{-}H) = 2.01$).

Appendix: Computer Simulation

Computational Method. The volume of a nonideal mixture is a complicated function of pressure, temperature, and composition. The molar volume of a fluid mixture is usually not a linear combination of the pure component molar volumes, due to the existence of excess volumes. Hence, the partial molar volume

---

(36) Exner, O. Empirical Calculations of Molar Volumes. In *Organic High Pressure Chemistry*; le Noble, W. J., Ed.; Elsevier: Amsterdam, 1988; p 19–49.

(37) The partial molar volume of butadiene (**13**) in toluene was determined from density measurements to be $V(\mathbf{13}) = 83.1$ cm^3/mol. Dogan, B. M. J. Ph.D. Dissertation, Universität Bochum, 1983.

(38) Bartlett, P. D.; Wallbillich, G. E. H. *J. Am. Chem. Soc.* **1969**, *91*, 409–414. We thank Professor M. Christl (University of Würzburg) for providing us with the modified procedure dealing with the preparative separation of the diastereomeric 1,4-dichloro-1,3-butadienes.

cannot be identified with the pure component molar volume or its van der Waals volume. The same criteria must be assumed for activation volumes. Again, activation volumes cannot be identified only with van der Waals volumes of transition states but configurational effects in the ensemble of the molecular states have to be taken into account. We have estimated these effects from isobaric Monte Carlo simulations (*NpT* ensemble: *N*, ensemble size; *p*, pressure; *T*, temperature). The molecules were modeled as rigid structures composed of fused hard spheres, where each atom was represented by a hard sphere. The same structural parameters—bond lengths, bond angles, and van der Waals radii—already used for the calculation of the van der Waals volumes were employed here. This is a very simplistic model, where conformational changes as well as intermolecular attraction forces are neglected. But, for the high pressures used in the experimental work reported here, the structure of fluids is dominated by the repulsive part of the interaction potential and the model of fused hard spheres is not inadequate for its description.

The simulation was carried out in a cubic box of variable size with periodic boundary conditions. The positions of molecules were selected at random, then moved and rotated by random increments. For the calculation of random numbers, we have used a 48-bit pseudorandom number generator supplied by our computer manufacturer (Hewlett-Packard) and destroyed eventual sequential correlations with a rehashing algorithm.[30] The new configuration was discarded, if the moved molecule overlapped with another molecule, or accepted, if this were not the case.

A fast algorithm for the calculation of interatomic distances has been reported earlier.[31] Even so, checking each atom of a pair of molecules consisting of 20 atoms for overlaps is an extremely time-consuming task. In order to save computer time, we have added the following improvements:

(1) For an ensemble of hard molecules, even one overlap is unacceptable. Once an overlap was detected, no further checking needed to be done and the configuration was discarded.

(2) A sequence list of neighbor molecules to be checked for overlaps was determined, maintained for each individual molecule, and updated after each move: a neighbor molecule that was found to have been the cause of an overlap was moved to the top of the sequence list. With this method, the first overlap could usually be detected after checking a few neighbor molecules instead of all $N - 1$ other molecules.

(3) For all molecules, the circumscribed and the inscribed spheres were calculated. If the circumscribed spheres do not overlap, no overlap of atoms is possible (this configuration is acceptable). If the inscribed spheres overlap, an overlap of some atoms is inevitable (this configuration is not acceptable). Only if the circumscribed spheres, but not the inscribed spheres, overlap does the time-consuming check for overlaps atom by atom need to be done.

(4) The distances between the circumscribed spheres were kept in a distance table and updated appropriately. Only molecules below a certain threshold were included in the check for overlaps.

After $N/4$ attempted moves, the volume was changed by a random factor. The new volume was accepted if the following condition was fulfilled:[32]

$$\exp\left(-\frac{U'-U}{k_BT}\right)\exp\left(-\frac{p(V'-V)}{k_BT}\right)\left(\frac{V'}{V}\right)^{3(N+1)} > \xi \quad (1)$$

Here ξ denotes a random number between 0 and 1. U denotes the internal energy, and V, the volume of the simulation ensemble. U' and V' refer to the ensemble after the volume change. Note that, for a hard molecule ensemble, the first exponential in relation 1 is 0, if the volume change creates an overlap, or 1 otherwise. The maximum sizes of the random displacements, rotations, and volume changes were adjusted dynamically to give the largest possible rms displacements, rotations, and volume changes. The acceptance ratio turned out to be 25–35%, in accordance with the observations of Kolafa.[33]

For an ensemble of hard molecules, temperature has no influence on fluid structure. We, therefore, used a dimensionless reduced pressure $\bar{p} = pu^3/k_BT$ in our simulations. Here, u denotes the unit length of the simulation (in this work, 1 Å). At ambient temperature, a p value of 0.1, roughly equivalent to 4 kbar, reproduces the properties of fluid liquids reasonably well. The simulations were initialized by placing the molecules with random orientation and coordinates into a very large volume. Then the reduced pressure was set to the desired value, and the volume change mechanism of the isobaric Monte Carlo method let the volume shrink and then fluctuate about its equilibrium value. At low pressure ($p = 0.03$), equilibrium was usually obtained after 2×10^6 attempted displacements and a reliable average density could be calculated from the next 4×10^6 moves. At higher pressures, equilibration runs of more than 8×10^6 and production runs of more than 1×10^7 moves were no exception. We observed that equilibration became difficult, and densities irreproducible, for reduced pressures above 0.1.

Simulation Results. A reliable calculation of partial molar volumes of a chemical compound by computer simulation requires a sufficiently large number of molecules to be present in the simulation ensemble. On the other hand, a large concentration of transition structures is unrealistic. As a compromise, we have used an ensemble size of 256 molecules for the mixture between the starting material and solvent (e.g., 256 butadiene molecules or 208 solvent molecules + 48 butadiene molecules) and of 232 molecules for the mixtures between transition or product structures and the starting material or solvent molecules (e.g., 208 unreacted butadiene or solvent molecules + 24 transition or product structures). Hence the product mole fraction is about 0.1, and the statistical weight of the product–product interaction, 0.01, which is sufficiently small. Simulations have been performed for the pericyclic Diels–Alder reaction of ethene with 1,3-butadiene (**13**) (Table 7) as well as for the dimerization of 1,3-butadiene (**13**) (Table 8). In the latter case, several reaction pathways have been explored. In addition, we have tried to show the influence of the solvent by studying the dimerization of butadiene (**13**) in an excess of **13** as well as of either very small or very large spherical molecules as solvent. We refer to these solvent molecules as helium and radon but do not insist that the molecular parameters used in this work reflect the real behavior of those gases nor that these gases should be used in kinetic experiments.

Since the equations of state of several hard molecule ensembles (spheres, dumbbells, convex bodies) are available from statistical thermodynamics, one might ask if it is possible to derive the desired mixture volumes from such an equation, instead of performing time-consuming computer simulations. The statistical thermodynamical equations of state generally have the following form:

$$Z = \frac{pV}{Nk_BT} = 1 + \frac{a_1\xi + a_2\xi^2 + a_3\xi^3}{(1-\xi)^3} \quad (2)$$

with $\xi = V_w/V_m$, the space filling fraction. The coefficients a_i are given in refs 34 and 35:

$$\begin{aligned} a_1 &= 3\alpha + 1 \\ a_2 &= 3\alpha^2 - 3\alpha - 2 \\ a_3 &= \begin{cases} 1 - \alpha^2 & \text{hard dumbbells} \\ 1 - \alpha(6\alpha - 5) & \text{hard convex bodies} \end{cases} \end{aligned} \quad (3)$$

The shape parameter α is the ratio of mean curvature radius, surface, and volume ($\alpha = rs/v$ and is 1 for spherical molecules. We have fitted eq 2 to our simulation results for helium, ethene,

Table 11. Coefficients of the Hard Dumbbell Eq 2[a]

substance		a_1	a_2	a_3	α
helium	fitted	4.034	−1.871	2.379	1.011
	recalculated	4.034	−1.965	−0.023	
	exact	4.000	−2.000	0.000	1.000
ethene	fitted	4.571	−1.863	0.311	1.190
	recalculated	4.571	−1.320	−0.417	
butadiene	fitted	7.322	−12.473	15.088	2.171
	recalculated	7.322	5.002	−3.411	

[a] Fitted: calculated from Monte Carlo results in **Tables 7** and **8**. Recalculated: calculated from α, using eq 3.

and butadiene, calculated α from a_1, and tried to recalculate a_2 and a_3 from this α value. The results are shown in Table 11. Of course, the statistical uncertainties of the simulated volumes lead to large error margins of the polynomial coefficients, especially for a_3. In the case of helium, the other fitted coefficients fulfill the relations 3, whereas the agreement is worse for ethene and nonexistent for the highly nonspherical butadiene. We conclude that the influence of molecular shape on the equation of state is large and too complicated for the recently available statistical thermodynamical theories of rigid molecules and that at present computer simulation is the only means of getting reliable volumetric data for these molecules.

The partial molar volumes are approximated by ratios of differences according to eqs 4 and 5. Consider, as an example, the reaction A + B → C in the presence of a solvent S. Let us assume that the molar volumes of the following ensembles have been obtained from simulation: $V^{\alpha}{}_{m}$, N_SS; $V^{\beta}{}_{m}$, N_SS + N_RA; $V^{\gamma}{}_{m}$, N_SS + N_RA + N_RB; $V^{\delta}{}_{m}$, N_SS + N_RC. In this work, we have used $N_S = 208$ and $N_R = 24$. The partial molar volumes of A, B, and C are then approximately

$$V_A \approx \frac{(N_R + N_S)V_m^{\beta} - N_S V_m^{\alpha}}{N_R}$$

$$V_B \approx \frac{(2N_R + N_S)V_m^{\gamma} - (N_R + N_S)V_m^{\beta}}{N_R}$$

$$V_C \approx \frac{(N_R + N_S)V_m^{\delta} - N_S V_m^{\alpha}}{N_R} \tag{4}$$

and the reaction volume is

$$\Delta V = V_C - V_A - V_B \approx \frac{(N_R N_S)V_m^{\delta} - (2N_R + N_S)V_m^{\gamma}}{N_R} \tag{5}$$

At this level of approximation, the molar volumes $V^{\alpha}{}_{m}$ and $V^{\beta}{}_{m}$ are evidently not required and the reaction volume is the difference of the absolute ensemble volumes, before and after the reaction, divided by the number of product molecules.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, and Fonds der Chemischen Industrie for financial support. We thank Professor Wolfgang R. Roth for providing us with a copy of the extended molecular mechanics program MM2ERW, Professor William von Eggers Doering and Professor Kendall N. Houk for sharing results in advance of publication and helpful comments, and Dr. Wolfgang Dietrich (Ruhr-Universität Bochum) and Mr. Heinz Bandmann (Universität GH Essen) for performing the NMR measurements.