was converted to 48 g (30%) of **21**: bp 96–98 °C (2 Torr) (lit.[5] bp 82–83 °C (0.7 Torr)); ^{1}H NMR (CCl_4) δ 1.4–2.6 (m, 12 H), 1.3 (s, 3 H), 5.5 (s, 1 H); IR (neat) 1670, 1595, 1450, 1325, 1255, 1205, 1190, 860 cm^{-1}.

2-Ethylidene-10-methyl-1(9)-octalin (19 and 20).[10] Dry dimethyl sulfoxide (DMSO, 10 mL) was added to 1.2 g (0.030 mol) of pentane-washed sodium hydride under nitrogen, and the mixture was stirred at 70 °C until hydrogen evolution ceased (45 min). The resulting slurry was cooled to RT, and 12.5 g (0.035 mol) of ethyltriphenyl phosphonium iodide (prepared in 73% yield from triphenylphosphine and ethyl iodide in toluene) was added followed by 25 mL of dry DMSO. The bright orange-colored mixture was stirred for 20 min at RT followed by dropwise addition of ketone **21** (4.10 g, 0.025 mol) in 25 mL of dry DMSO over a period of 15 min. The resulting mixture was stirred at 60 °C for 36 h and cooled to RT, and 50 mL of pentane followed by 50 mL of H_2O was added to the mixture. The triphenylphosphine oxide was removed by filtration, and the filtrate was extracted with 4 × 100 mL of pentane. The combined pentane extracts were washed with 3 × 100 mL of 1:1 H_2O/DMSO and dried, and the pentane was removed by rotary evaporation. Distillation afforded 2.65 g (60.2%) of *cis*- and *trans*-2-ethylidene-10-methyl-1(9)-octalin (**19** and **20**, respectively): bp 90–92 °C (2 Torr).

Kinetics of the Diels–Alder Addition of Maleic Anhydride to the 1-(1-Propenyl)cycloalkenes. An NMR tube containing maleic anhydride (11.3 mg, 15.3 mmol), 4 mL of $CDCl_3$, and 10 μL of $CHCl_3$ was equilibrated in the variable-temperature probe of the EM-390 spectrometer at the desired temperature (calibrated by using the ethylene glycol peak shift method). To this tube was added 15.3 mmol of the desired diene. The decrease in the maleic anhydride peak height, with the $CHCl_3$ peak height as a standard, was followed. The second-order rate constants for these reactions, employing equal concentrations of diene and maleic anhydride, were determined by using the following equation:

$$1/(d - x) - 1/d = kt$$

where d is the initial concentration of maleic anhydride and x is the amount of maleic anhydride reacted at time t. The slope of a plot of $1/(d - x)$ vs t provides the second-order rate constant.[35] The adducts were not isolated, but they showed characteristic ^{1}H NMR peaks for the alkene proton at δ 5.6–5.7 in the adducts from **6** and **8** and at δ 5.2–5.3 in the adducts from **12** and **13**. All of the adducts showed the protons α to the carbonyl groups at δ 3.2–3.4. Finally, the saturated methyls appeared as doublets at δ 1.12 in the adducts from **6** and **12** while they appeared at δ 1.24 and δ 1.42 in the adducts from **13** and **8**, respectively.

Acknowledgment. This work was supported, in part, by a grant from the Research Corp. We also thank L. Scott Gilliam, Douglas Manatt, and Harvey Yamane for experimental assistance.

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Pressure-Induced Diastereoselectivity in Photoinduced Diels–Alder Reactions[†]

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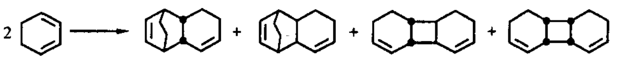
The product distributions for the photochemical electron transfer and triplet–triplet energy-transfer-induced dimerization of 1,3-cyclohexadiene (CHD) were determined as a function of pressure and solvent in the range of 0.1–203 MPa. In the case of the photochemically (dicyanonaphthalene sensitized) induced electron-transfer dimerization, differences in activation volumes for the formation of *endo*-1 and *exo*-2 adduct are small and positive in acetonitrile (ca. +1 to +2 cm^3/mol) but are negative and unusually large (ca. −9 to −12 cm^3/mol) in benzene. The results are consistent with the involvement of different types of solvated ion pairs in the two solvents. Although the product distribution does not change for any of the sensitizers and pressures used in the triplet-sensitized reaction, the efficiency of dimerization was surprisingly both pressure and solvent dependent. The activation volumes for efficiency of dimerization of CHD by triplet–triplet energy transfer fall in the range −22 to +2.1 cm^3/mol and depend on both the triplet energy of the sensitizer and the solvent used.

Introduction

The dimerization of 1,3-cyclohexadiene (CHD) has been investigated (eq 1 and Table I) under a variety of conditions.[1-3] The thermal dimerization requires long reaction times and produces a mixture of the *endo*-1 and *exo*-2 Diels–Alder adducts (eq 1) in poor yield. In contrast, the dimerization of CHD induced by means of radical cation catalysis produces good yields of the Diels–Alder adducts.[2,3] In the latter case, both thermal electron acceptors and



endo-1 exo-2 anti-3 syn-4

(1)

[†] This paper is part 22 of the Aachen-series "Radical Ions and Photochemical Charge Transfer Phenomena". For part 21 see ref 3a.

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Table I. Reaction Conditions and Product Ratios in the Dimerization of CHD

entry	method	yield, %	products endo	exo	anti	syn	ref
1	Δ	32	4	1			1a,1b
2	*hν*, direct			1	4.4	2.3	1c
3	*hν*, triplet	92	trace	1	3	1	1b
4	*hν*, DCN, MeCN[a]	80	6	1	minor	pdts	4b
5	*hν*, DCN, MeCN[b]	94	14	1	minor	pdts	3a
6	*hν*, DCA, MeCN[c]	60	3.3	1			1f
7	*hν*, TPP^+, CH_2Cl_2[d]	82	6	1			3d
8	*hν*, TPP^+, CH_2Cl_2[e]	98	10	1			3a
9	e^-, $MeCN/CH_2Cl_2$ (1:1),[f] $LiClO_4$	24	28	1			3d
10	Δ, $\text{TBPA}^{+\circ}$, CH_2Cl_2[g]	77	4	1			2

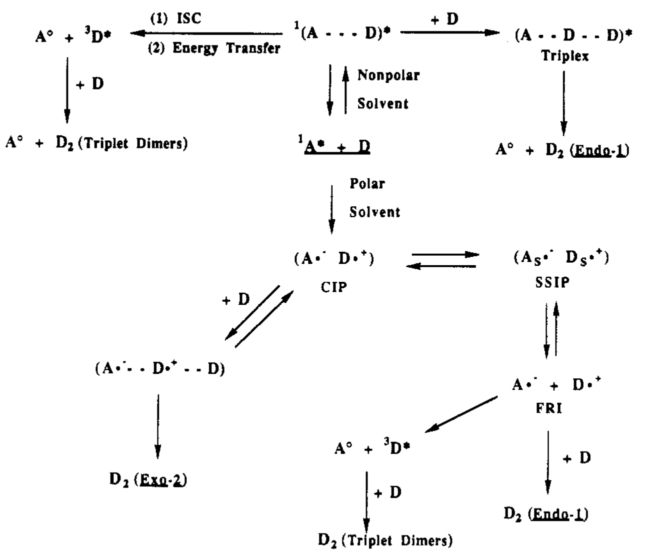
[a] DCN = 1,4-dicyanonaphthalene, 2.1 M CHD. [b] 0.1 M CHD. [c] DCA = 9,10-dicyanoanthracene. [d] TPP^+ = 2,4,6-triphenylpyrylium BF_4^-; with trityl BF_4^- the yield is 95% and endo:exo is 8:1; 0.125 M CHD. [e] 0.05 M CHD. [f] Electrochemically induced. [g] $\text{TBPA}^{+\bullet}$ = tris(*p*-bromophenyl)aminium hexachlorostibnate.

photochemical electron acceptors appear to operate through various processes.[1] Photochemical electron acceptors act as electron-transfer sensitizers, possibly through a chain reaction.[3a–c] For a decade the alternative thermal electron acceptor method was assumed to operate through a typical chain process.[2a–c,3d] However, recent results support a conventional catalytic mechanism for the dimerization of CHD.[2d] Under comparable reaction conditions, the stereoselectivity (*endo*-**1**/*exo*-**2** ratio of the Diels–Alder adducts) of thermal and electron-transfer sensitized dimers is about 4/1.[2,3] However, in the latter case the selectivity strongly depends on the diene concentration, favoring the *endo*-**1** isomer at very low concentrations.[3] Dimerization under triplet–triplet energy-transfer conditions yields mainly the *anti*-**3**, *syn*-**4**, and *exo*-**2** adducts.[1b] The product ratios are not dependent on the sensitizer energy or structure.

It has been shown that contact ion pairs on the one hand and solvent-separated ion pairs or free-radical ions on the other hand show different selectivities in the photochemical electron-transfer-induced dimerization of CHD (Scheme I).[3] While a high concentration of CHD in polar solvents favors the formation of the *exo*-**2** dimer, a lower concentration of CHD preferentially yields the *endo*-**1** adduct. Quenching experiments using 1,2,4-trimethoxybenzene and methanol confirm the involvement of differently solvated radical ion pairs: both 1,2,4-trimethoxybenzene and methanol efficiently quench the *endo*-**1** more than the corresponding *exo*-**2**, suggesting the trapping of free-radical ions but not the contact ion pairs (Scheme I).[3] In nonpolar solvents, high concentrations of CHD favor *endo*-**1** adduct, via trapping of an exciplex.[1f,4]

Pressure variation provides a useful mechanistic tool for the investigation of photochemical mechanisms.[5] For example, it has been demonstrated that the activation volume, $\Delta V^{\ddagger}$, derived from the pressure dependence of the rate constant of the reaction, is a useful criterion for classification of cycloaddition reaction mechanisms.[6]

Scheme I[a]



[a] A = 1,4-dicyanonaphthalene; D = CHD; CIP = contact ion pairs; ISC = intersystem crossing; SSIP = solvent-separated ion pairs; FRI = free-radical ions.

Thus, ambiguities of photochemical mechanisms of cycloaddition reactions may be investigated and elucidated with this pressure technique. Previous work on the pressure dependence of the thermal dimerization of CHD showed[7] that the *exo*-**2** adduct is formed through a nonconcerted Diels–Alder mechanism with an activation volume of $-22\ cm^3/mol$ and that *endo*-**1** and *exo*-**2** dimers have no common intermediate. Under certain thermal conditions, a novel [6+4]ene reaction was also observed. The activation volume for formation of the *endo*-**1** dimer is $-28\ cm^3/mol$, which is typical for a concerted mechanism. Recently, Tietze et al.[8] have succeeded in using high pressure to induce a significant degree of diastereroselectivity in a hetero-Diels–Alder reaction of an enamino ketone with ethyl vinyl ether. They found a remarkably large difference in activation volume ($\Delta\Delta V^{\ddagger}$) between the re-

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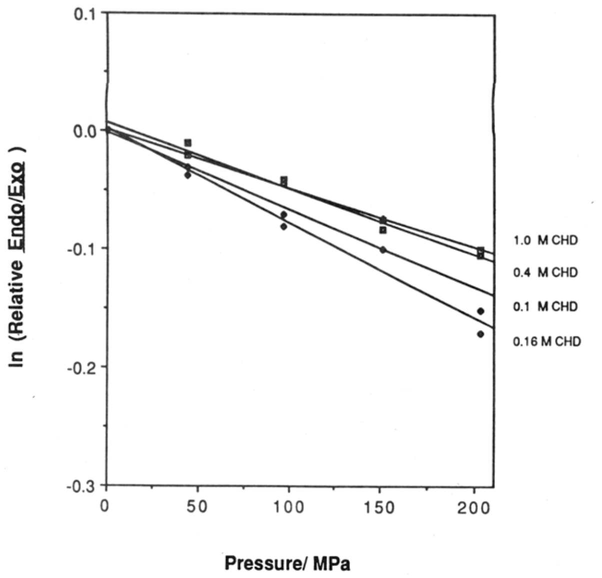

Figure 1. Pressure dependence on the ln (relative endo/exo ratio) of 1,4-dicyanonaphthalene-sensitized dimerization of CHD in MeCN at 25 °C. From top to bottom lines, the $\Delta\Delta V^{\ddagger}$ are in the range 1.2–2.4 cm^3/mol.

action paths leading to the two diastereomers: 5.8 cm^3/mol.

We report here that for the photochemically induced dimerization of CHD, an even more significant increase of diastereoselectivity can be obtained by applying high pressure, that pressure effects provide a criterion for differing mechanisms of cycloaddition in different solvents, and that an unanticipated energy-dependent pressure effect exists for the efficiency of dimerization under triplet-sensitized conditions.[9]

Experimental Section

1,4-Dicyanonaphthalene was prepared according to a literature method[10] and recrystallized from acetonitrile. CHD (Aldrich) was distilled under argon before use. Acetophenone (Aldrich), 2-acetonaphthone (Aldrich), 1-acetonaphthone (Aldrich), benzil (Baker), benzophenone (Baker), and phenanthrene (Aldrich) were used as received. Spectroscopic grade methylcyclohexane (Aldrich), benzene (Aldrich), and acetonitrile (Kodak) were used without further purification. The samples were degassed by purging with nitrogen for 10 min prior to irradiation. The high-pressure instrument has been described previously.[5f] A circulating water supply maintained the sample chamber at 25.0 ± 0.5 °C during irradiation. The dimers were analyzed by capillary gas chromatography (Hewlett-Packard 5890, column HP-1, 25 m) and identified by comparing retention times with independently prepared samples.[1b,2] The irradiations were carried out employing the output of a Xe/Hg high-pressure lamp (1 kW) passed through a K_2CrO_4 filter solution and were controlled in order to have the same irradiation period. At least two measurements were taken for each sample. The variation of the *endo*-**1** to *exo*-**2** ratio for different runs was less than 5%.

Linear least-squares analysis (eq 2) was used[6,11] to obtain the volume of activation at zero pressure. In cases where data could not be fit by the linear function (eq 2), the quadratic function $\ln k = a + bp + cp^2$ was used.[6,11,12]

$$(\partial \ln k/\partial p)_T = -\Delta V^{\ddagger}/RT \qquad (2)$$

Table II. 1,4-Dicyanonaphthalene-Sensitized Dimerization of CHD in MeCN at 25 °C

press., MPa	1.0 M CHD^a endo/exo	0.4 M CHD^a endo/exo	0.16 M CHD^a endo/exo	0.1 M CHD^a endo/exo
0.1	5.7	5.6	9.2	13.0
44	5.6	5.4	9.2	12.6
97	5.4	5.2	8.8	12.0
151	5.3	5.2	8.5	11.7
203	5.1	4.8	8.3	10.9
$\Delta\Delta V^{\ddagger}$ cm^3/mol	1.2	1.6	2.4	2.0

^{a} 0.02 M 1,4-dicyanonaphthalene in acetonitrile; errors <10%.

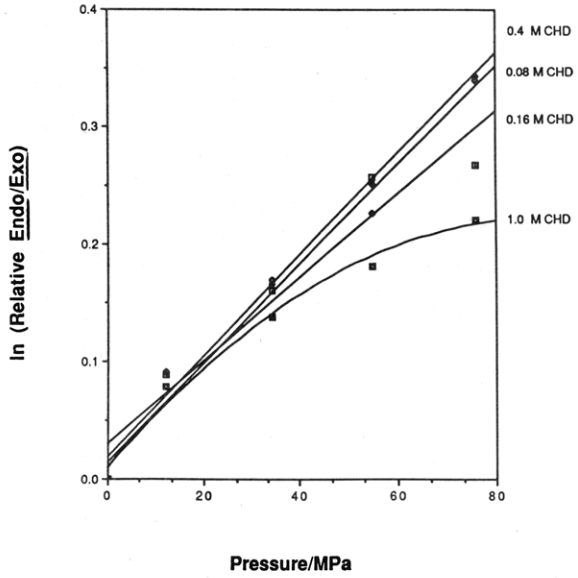

Figure 2. Pressure dependence on the ln (relative endo/exo ratio) of 1,4-dicyanonaphthalene-sensitized dimerization of CHD in benzene at 25 °C. Values of the observed $\Delta\Delta V^{\ddagger}$ range from −11.6 to −8.7 cm^3/mol.

Results

Photochemical Electron-Transfer-Induced Dimerization of CHD. Irradiation of 1,4-dicyanonaphthalene (2.0×10^{-2} M) in a degassed *acetonitrile* solution containing 0.16 M CHD gives both *endo*-**1** and *exo*-**2** dimers in a ratio of 9.2:1 and the *anti*-**3** and *syn*-**4** dimers in a ratio of approximately 3:1. The *endo*-**1** and *exo*-**2** dimers comprise more than 86% of the dimer mixture at low conversion (<10%). The ratio of *endo*-**1** to *exo*-**2** decreases at high concentrations of CHD from a value of 13 (0.1 M CHD) to 5.6 (0.4–1 M CHD); it also decreases as a function of pressure with $\Delta\Delta V^{\ddagger}$ = +1.2 to 2.4 cm^3/mol (Figure 1). The percentage of [4+2] dimers decreases slightly with increasing pressure. The results show that the *exo*-**2** dimers are favored over the *endo*-**1** dimers at both high concentration of CHD and high pressure. In the concentration range of CHD studied (0.1–1 M), the yield of dimers (for equal doses of absorbed light) slightly decreased with pressure. The results are summarized in Table II.

Contrasting results are obtained for the photochemical electron-transfer-induced dimerization of CHD with 1,4-dicyanonaphthalene in a nonpolar solvent, *benzene*. Both [4+2] dimers and [2+2] dimers are produced; however, the

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(9) The results have already been presented in the (a) 10 Vortragstagung der GDCH-Fachgruppe Photochemie, Würzburg (West Germany), Nov 18–20, 1987, Proceedings pp 165–167 and (b) XII IUPAC Symposium on Photochemistry, Bologna, July 17–22, 1988, Proceedings pp 605–606. (c) Sixth Symposium on Photochemistry, Eisenach, GDR, Sept. 18–30, 1988, Proceedings p 136.

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Table III. 1,4-Dicyanonaphthalene-Sensitized Dimerization of CHD in Benzene at 25 °C

	1.0 M CHD[a]		0.4 M CHD[a]		0.16 M CHD[a]		0.08 M CHD[a]	
press, MPa	endo/exo	%[b]	endo/exo	%[b]	endo/exo	%[b]	endo/exo	%[b]
0.1	1.62	56.3	1.05	44.1	0.75	37.8	0.59	36.7
12	1.74	58.6	1.15	46.0	0.82	39.5	0.64	37.6
34	1.86	61.0	1.24	48.0	0.88	41.2	0.70	39.5
55	1.93	62.5	1.35	50.1	0.97	42.7	0.74	41.0
76	2.02	64.2	1.48	53.5	0.98	44.8	0.83	42.9
$\Delta\Delta V^{\ddagger}$ (cm^3/mol)	-11.6[c]	-6.2[c]	-10.7	-5.9	-8.7	-5.2	-11.1	-5.0

[a] 0.02 M 1,4-Dicyanonaphthalene in benzene; errors <10%. [b] % yield of endo plus exo relative to all dimers. [c] Data were fit by quadratic function.

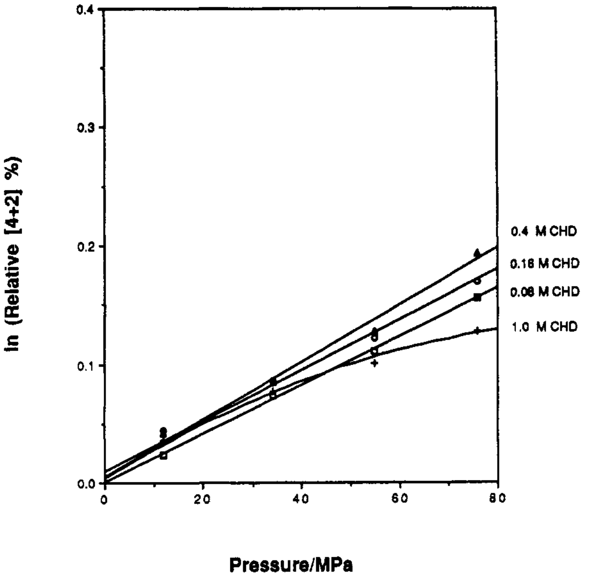

Figure 3. Pressure dependence on the ln (relative [4+2] %) of 1,4-dicyanonaphthalene-sensitized dimerization of CHD in benzene at 25 °C. The observed $\Delta\Delta V^{\ddagger}$ are in the range -6.2 to -5.0 cm^3/mol.

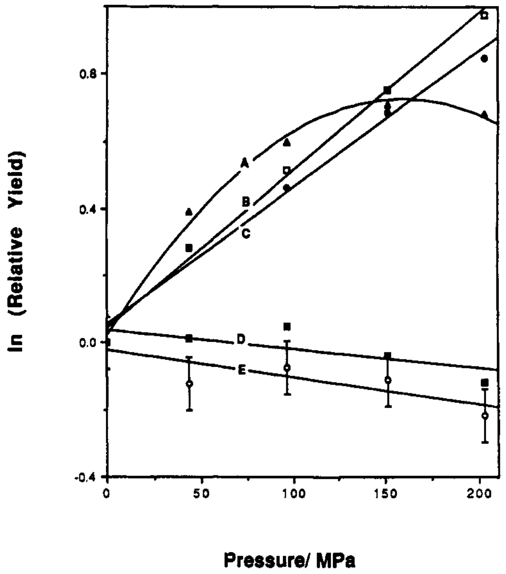

Figure 4. Plot of ln (relative yields) vs pressure in the triplet-sensitized dimerization of CHD in methylcyclohexane at 25 °C: A (BZP); B (ACP); C (PhN); D (BZL); E (2-ACN). Abbreviations same as those in Table IV, footnote *a*.

ratio of *endo*-1 to *exo*-2 increases significantly at high concentration of CHD from a value of 0.59 (0.08 M CHD) to 1.62 (1.0 M CHD). The *endo*-1 to *exo*-2 ratio also increases with pressure, giving an average activation volume difference, $\Delta\Delta V^{\ddagger}$, of -10 cm^3/mol (Figure 2).[13] The percentage of [4+2] dimers increases with both high pressure and/or high concentration of CHD with a $\Delta\Delta V^{\ddagger}$ from -5.0 cm^3/mol (0.08 M CHD) to -6.2 cm^3/mol (0.4 M CHD; Figure 3). The total yield of dimers (for constant doses of absorbed light) remains constant (±5%) in the range of pressure studied (0.1-80 MPa). The results are summarized in Table III.

Triplet-Sensitized Dimerization. The influence of pressure on the triplet-sensitized dimerization[1b] of CHD was examined as a function of triplet sensitizers of varying energy and of solvent polarity. The triplet-sensitized dimerization, irrespective of sensitizer and solvent, has been shown[1b] to produce *exo*-2, *anti*-3, and *syn*-4 dimers (eq 1) in a ratio of 1:3:1. Only traces of *endo*-1 dimers are formed. We have confirmed these results and found that the ratio of products is independent of pressure under the condition investigated. In addition to *endo*-1, *exo*-2, *anti*-3, and *syn*-4 dimers an unknown dimer less than 1.5% was also observed, which could be a stereoisomer of these products.[1g,7]

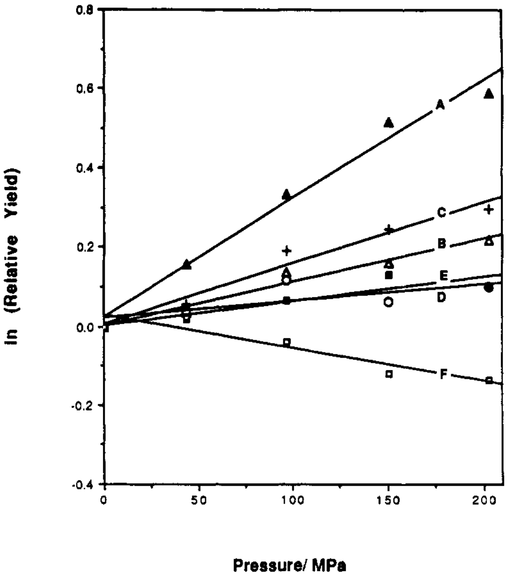

Figure 5. Plot of ln (relative yields) vs pressure in the triplet-sensitized dimerization of CHD in MeCN at 25 °C: A (ACP); B (BZP); C (PhN); D (2-ACN); E (1-ACN); F (BZL). Abbreviations same as those in Table IV, footnote *a*.

However, for a comparable dose of irradiation in methylcyclohexane, *pressure increases the yield of dimers* (Figure 4) with an activation volume of -12 cm^3/mol for acetophenone and -10 cm^3/mol for phenanthrene, corresponding to an activation volume typical for a single-bond formation.[6,12] For benzophenone the activation volume of the formation of dimers was determined to be -22 cm^3/mol. In the cases of 2-acetonaphthone and benzil, however,

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[13] To our knowledge this is currently the highest activation volume difference measured in Diels-Alder reactions. For $\Delta\Delta V^{\ddagger}$ = -5.8 cm^3/mol measured for a hetero-Diels-Alder reaction see ref 8.

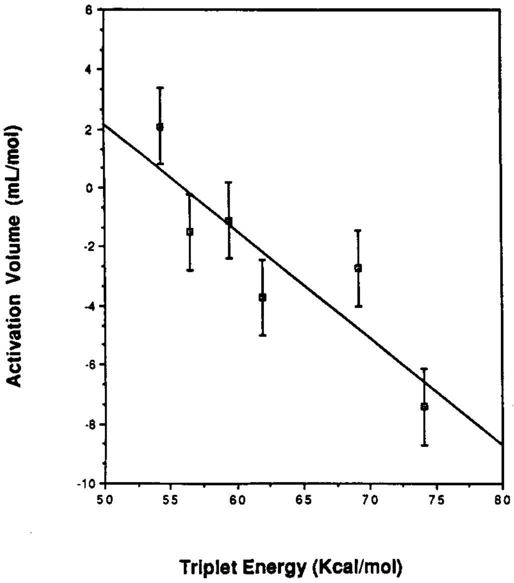

Figure 6. Plot of the observed activation volumes vs triplet energy of sensitizers used in the triplet-sensitized dimerization of CHD in MeCN.

Table IV. Triplet-Sensitized Dimerization of 0.16 M CHD in Methylcyclohexane at 25 °C

	yield, %				
press., MPa	BZP[a]	ACP[a]	PhN[a]	2-ACN[a]	BZL[a]
0.1	5.5	2.6	3.3	9.0	6.7
44	7.8	3.4	4.4	8.0	6.8
97	9.9	4.3	5.3	8.4	7.0
151	11	5.5	6.6	8.1	6.4
203	11	6.8	7.8	7.3	6.0
$\Delta V_{\mathrm{obs}}^{\ddagger}$, cm^3/mol	−22[b]	−12	−10	+2.0	+1.4

[a] 0.02 M sensitizer in methylcyclohexane, errors about 15%. BZP, benzophenone; ACP, acetophenone; PhN, phenanthrene; 2-ACN, 2-acetonaphthone; BZL, benzil. [b] Data were fit by quadratic function.

pressure-retarded dimerizations, corresponding to positive activation volumes for the efficiency of dimerization of CHD, were observed (Figure 4). Qualitatively, sensitizers of higher triplet energy show negative activation volume, while sensitizers of lower energy show positive activation volume.

In acetonitrile the pressure effect on the yield of dimers shows a clearer correlation with triplet energy, E_T, of the sensitizers (Figures 5 and 6); as for the results in methylcyclohexane, for higher triplet energies, the activation volume is more negative. Acetophenone (E_T = 74.1 kcal/mol) shows an activation volume of −7.4 cm^3/mol, and benzophenone (E_T = 69.2 kcal/mol) shows an activation volume of −2.7 cm^3/mol. 1-Acetophenone (E_T = 56.5 kcal/mol) and 2-acetophenone (E_T = 59.4) kcal/mol) sensitized reactions however show only a small increase on the efficiency of dimerization by pressure. In the case of benzil (E_T = 54.3 kcal/mol), a pressure-retarded sensitized dimerization was observed with a +2.1 cm^3/mol activation volume. The product distributions did not change in any of these cases. The results are summarized in Tables IV and V.

Discussion

The activation volume at zero pressure, $\Delta V^{\ddagger}$, cannot be estimated with reasonable accuracy unless very precise data free of systematic errors are available over a range of moderate pressures to permit extrapolation of $\partial \ln k/\partial p$. However, differences in volume of activation for various dimers (such as *endo*-1, *exo*-2) can be estimated with much greater precision.[8,14] Values of $\Delta\Delta V^{\ddagger}$ calculated by extrapolating the slopes of ln (relative ratio) versus pressure are independent of any errors in absolute rate measurements and are accurate within 1 cm^3/mol.

Table V. Relative Yield of Triplet-Sensitized Dimerization of 0.16 M CHD in MeCN at 25 °C

	yield, %					
press., MPa	ACP[a] (74.1)[b]	BZP[a] (69.2)[b]	PhN[a] (62.0)[b]	2-ACN[a] (59.4)[b]	1-ACN[a] (56.5)[b]	BZL[a] (54.3)[b]
0.1	3.8	10.4	9.4	13.6	11.1	13.2
44	4.4	10.8	10.0	14.6	11.3	14.2
97	5.2	12.0	11.4	15.4	11.8	13.4
151	6.4	12.2	12.0	14.6	12.7	13.2
203	6.8	13.0	12.8	15.0	12.4	12.0
$\Delta V_{\mathrm{obs}}^{\ddagger}$ (cm^3/mol)	−7.4	−2.7	−3.7	−1.1	−1.5	+2.1

[a] 0.02 M sensitizer in MeCN, errors about 15%. Abbreviations are the same as those in Table IV, footnote *a*. [b] Triplet energy of the sensitizers used, in unit of kcal/mol. Triplet energy data were taken from Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

Photochemical Electron-Transfer-Induced Dimerization of CHD. The mechanistic pathways required for discussion of the photochemical electron-transfer-induced dimerization of CHD are shown in Scheme I. It has been reported that the contact ion pair, which is formed after the initial electron transfer, is quenched by means of a high concentration of CHD which mainly leads to the *exo*-2 dimers.[3a–c] Dissociation into free-radical ions occurs at low concentration of CHD and leads mostly to the *endo*-1 dimer.[3a–c] The radical cation of CHD can be generated electrochemically and leads to a high selectivity of endo to exo dimers.[3d] In a fundamental study Farid[15] demonstrated that different reactivities of radical ion pairs and free-radical ions in the dimerization of 1,1-diphenylethene leads to the cyclobutanes and the [4+2] dimers. These results are consistent with the involvement of two different types of ion pairs in the mechanisms.

Thus, the photochemical electron-transfer-induced dimerization of CHD appears to occur by two distinct mechanisms.[3a–c,4] First, in the mechanism that operates in *nonpolar solvents*, an exciplex is involved, and the endo/exo ratio is *increased* by application of both high pressure and/or high concentration of CHD. Second, in the mechanism that operates in *polar solvents*, electron transfer to form radical ion pairs is involved, and the endo/exo ratio is *decreased* by application of both high pressure and/or high concentration of CHD. The endo/exo ratio decreases with pressure in polar solvents with $\Delta\Delta V^{\ddagger}$ = +1.2 to 2.4 cm^3/mol but increases with pressure in nonpolar solvents with $\Delta\Delta V^{\ddagger}$ = −10 cm^3/mol.[13]

We seek to explain the contrasting results in pressure effects for photochemical electron-transfer-induced dimerization in the solvents acetonitrile and benzene in terms of Scheme I. In polar solvent, the concentration dependence as well as the pressure dependence of the endo/exo ratio shows the involvement of different kinds of ion pairs in the formation of these dimers, since if both *endo*-1 and *exo*-2 were formed from the same intermediate or transition state, they would not show any pressure and concentration dependence. However, we find that the *exo*-2 adduct is favored by both high concentrations of CHD and pressure, which is consistent with the mechanism[3a–c] for the involvement of different ion pairs (contact ion pair leading to *exo*-2 and solvent-separated ion pair leading to *endo*-1) as shown in Scheme I. The effect of

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(15) Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1986**, *108*, 7356.

pressure can be understood qualitatively as resulting from the acceleration of the dissociation of the contact ion pair into solvent-separated ion pairs (solvent-separated ion pairs are more capable of solvation).[11b,12] Concurrently, the efficiency of trapping of contact ion pair by CHD also increases with pressure. The small effect of pressure on the [4+2] to [2+2] dimers as well as the small effect of pressure on the yield of dimers is attributed to competing and compensating effects on dissociation steps of the several intermediates.

In benzene, the electron transfer within the donor–acceptor complex is an endergonic process according to calculations from the Weller[16] equation and is therefore thermodynamically "forbidden". A donor–acceptor exciplex is formed in preference to ion pairs and is quenched by a high concentration of CHD to form a so-called triplex[1f,4] intermediate as shown by Calhoun and Schuster.[4] The product derived from the triplex is mainly the *endo*-**1** dimer and a small amount of *exo*-**2** adduct. From the concentration and pressure studies of the dimerization of CHD, the triplex mechanism may be relatively favored over the energy-transfer process at high pressure and high concentration of CHD applied (Scheme I). At low concentrations of CHD, intersystem crossing or energy transfer from the singlet exciplex to the triplet excited CHD competes with the triplex formation. The contribution of triplet dimers (*exo*-**2**:*anti*-**3**:*syn*-**4** = 1:3:1) percentage decreased as CHD concentration and pressure increased. The decrease in the *exo*-**2** dimer to *endo*-**1** dimer with increasing pressure is qualitatively understood as resulting from the retardation of the dissociation of the exciplex into triplet CHD and ground-state sensitizer (which requires an increase in volume). The longer lifetime of the exciplex causes its efficiency of trapping by CHD to increase with increasing pressure. The increase in the ratio of [4+2] to [2+2] dimers with pressure is also a natural consequence of the more efficient trapping of the exciplex by CHD, which leads to the triplex, the precursor of the *endo*-**1** dimer as a major product. The small effect of pressure on the efficiency of the yield of dimers is attributed to competing retarding effects on dissociation of the triplex and exciplex.

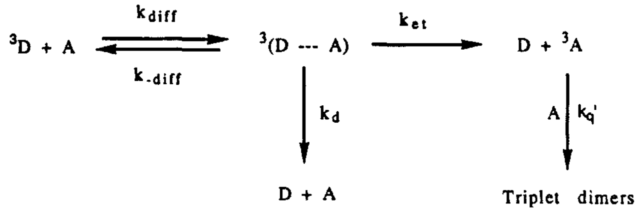
The activation volume differences, $\Delta\Delta V^*$, determined from the pressure dependence of *endo*-**1**/*exo*-**2** ratio are shown to be a small positive value in polar solvent but a large negative value in nonpolar solvent. Thus, the opposite sign of $\Delta\Delta V^*$ provides us with an unambiguous way of differentiating between the two distinct mechanisms in the photochemical electron-transfer-induced dimerization of CHD.

Triplet-Sensitized Dimerization. The increase in efficiency of dimer formation under pressure correlates with the triplet energy of the sensitizer as shown in Figure 6. This intriguing correlation in triplet-sensitized dimerization of CHD between activation volumes for the efficiency of dimer formation and ΔE_T could have its origins from several sources including solvent viscosity, polarity, involvement of different intermediates, and energy effects on energy transfer.

The generally accepted scheme[17] for the triplet-sensitized dimerization is shown in Scheme II. In this scheme, D is a donor, A is an acceptor, and ^{3}(D- - -A) is an intermediate, encounter complex, or exciplex with perhaps a specific configuration by way of which the forward and backward energy transfer and also the energy-dissipation process can occur. The observed rate constant for quenching (k_{ob}) of D* by A and the rate constant for energy transfer can be formulated as eq 3, where $\alpha = k_{et}/(k_{et} + k_d + k_{-diff})$. In other words, the observed rate constant (k_{ob}) for quenching of D* depends on (i) the rate constant for diffusion (k_{diff}) of D* and A together and (ii) the probability (α) that energy transfer will occur during the lifetime of the exciplex or encounter complex. On the assumption that product formation through the triplet CHD is not changed by pressure (an assumption justified by the insensitivity of product ratio to pressure), we can define the origin of the pressure effects on the efficiency of dimer formation to the rate of energy transfer.

$$k_{ob} = \frac{k_{diff}k_{et}}{k_{et} + k_d + k_{-diff}} = \alpha k_{diff} \qquad (3)$$

Scheme II



Consider two limiting situations in the energy-transfer processes: (1) The rate of dissociation of the exciplex or encounter complex is very fast relative to energy transfer ($k_{-diff} \gg k_{et}$). (2) The rate of dissociation of the exciplex or encounter complex is slow compared to energy transfer ($k_{et} \gg k_{-diff}$). Under these limiting conditions the observed rate constant for the triplet-sensitized dimerization becomes as follows: case 1 $k_{ob} = (k_{diff}/k_{-diff})k_{et}$ if $k_{-diff} \gg k_{et}$; case 2 $k_{ob} = k_{diff}$ if $k_{et} \gg k_{-diff}$.

When the energy difference between the triplet donor and acceptor decreases to about 4 kcal/mol, back transfer of triplet energy becomes important,[18,19] assuming that significant relaxation of the acceptor triplet does not occur following the energy-transfer process. For diffusion-controlled energy transfer, Schmidt et al.[20] have found that the yield of energy transfer from acetone to 9-bromoanthracene (BA) *decreases* with the application of pressure. Their study showed a difference in triplet energy of 2 kcal/mol between the acetone triplet and the accepting state (e.g., the T_2 state of BA). These results are consistent with our observation in the case of *benzil*-sensitized dimerization of CHD ($\Delta E_T \sim 2$ kcal/mol): both systems show *positive* activation volumes for the energy-transfer processes.

Sandros[18] proposed that the encounter complex is formed with a diffusion-controlled rate and that the probability for the forward and backward energy transfer is determined *only by the energy difference* between the triplet donor (D) and acceptor (A). Wagner,[17b] on the other hand, studied systems in which energy transfer is irreversible and obtained results that lead to the conclusion that *the transfer efficiency can be much smaller than diffusion-controlled* because of the competition between

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the transfer process and the diffusional separation of ^3D and A. Other researchers have found systems for which triplet energy transfer, which strongly exothermic, still occurs well below the diffusional rate.[21,22,25] The latter results could provide a clue to explain our observation of the pressure dependence of triplet energy transfer with a larger energy difference.

The triplet energy of CHD has been estimated[1b] to be about 52 kcal/mol. As the sensitizer triplet energy approaches the triplet excitation energy of CHD, the activation volumes approach those (small positive values) expected for diffusion control, and the reaction efficiency begins to decrease with increasing pressure. Thus, we interpret the results for the lower energy sensitizers as representing cases for which we approach the limiting case 2, for which $k_{ob} = k_{diff}$. Accordingly, for the higher energy sensitizers, we interpret the results to be limited in case 1, for which $k_{ob} = (k_{diff}/k_{-diff})k_{et}$. Of the three components of k_{ob}, evaluation of k_{diff} as a function of pressure should yield a positive activation volume, since pressure is well-known to increase solvent viscosity and therefore to slow down the rate of diffusion. Of the two remaining terms, k_{et} is a unimolecular process of energy transfer within an encounter complex or exciplex, and k_{-diff} is a unimolecular process of dissociation of an encounter complex or exciplex. The pressure effect on k_{et} is expected to be small (no significant change in volume for the internal energy transfer, since no bonds are being formed or broken), whereas increasing pressure is expected to *decrease* k_{-diff}. As a result, k_{ob} is expected to *increase* with pressure, as observed for the high-energy sensitizers. What remains to be explained is why there is a sensitizer energy effect in the high-energy region.

One possible speculative explanation, which has not been typically observed in the literature, is that there is "Marcus inverted region" for triplet energy transfer.[23-25] Thus, we propose that *higher energy triplet donors do not transfer at the diffusional rate*[25] *because they have too much excess energy of which to dispose* or, in terms of the Marcus formulation, because the electronic coupling is smaller as the excess energy increases. This would make the magnitude of k_{et} smallest for the highest energy sensitizers. As a result, the ratio of rates given by k_{et}/k_{-diff} would be subject to the largest influence of pressure if the disposal of electronic energy requires electronic or organizational effects that are opposed by increasing pressure. As the energy of the triplet donor becomes closer to that of CHD, the transfer becomes more efficient, the pressure effect begins to diminish in magnitude, and eventually a situation typical of diffusion control is achieved. Although further work is needed, in particular the dependence of the absolute rate constants for triplet energy transfer on pressure before the validity of this interpretation can be tested in detail, recent evidence has begun to suggest the possibility of an inversion region for exchange energy transfer.[24a]

Conclusion

The effects of pressure on the photochemical electron-transfer-induced dimerization of CHD show the following: (1) A large difference exists in the activation volume, $\Delta\Delta V^{\ddagger}$ (10 cm^3/mol in benzene) for formation of *exo*-**2** dimers relative to *endo*-**1** dimers, so that significant control of diastereoselectivity is possible by application of high pressure at constant temperature. (2) In polar and nonpolar solvents the pressure dependence of the *endo*-**1** to *exo*-**2** ratio on applied pressure has an opposite sign of activation volumes, showing unambiguously that there are two types of mechanisms operating in the photochemical electron-transfer-induced dimerization of CHD.

Although the product distribution in the triplet-sensitized dimerization does not change for any of the sensitizers and solvents over the pressure range examined, the efficiency of dimerization is both pressure and solvent dependent. An unexpected and clearcut correlation between reaction activation volumes and differences in triplet energy was observed in acetonitrile (a similar trend was noted in methyl cyclohexane) and is provisionally attributed to the Marcus inverted region control of the rate of energy transfer within encounter complexes of triplet donor and triplet energy acceptors.

The results reported here may be related to two other reports on the effect of pressure on reactive organic intermediates. In one of these investigations the effect of pressure on the efficiency of collapse of a reversibly formed singlet exciplex (between adamantanone and 1,2-dicyanoethylene) to oxetane[5a] was investigated, and in the second investigation the effect of pressure on the efficiency of collapse of a reversibly formed complex between a carbene and ethylene[5b] was investigated. In each case the effect of pressure was attributed to retardation of dissociation of a reversibly formed complex, precisely the key concept proposed to rationalize the results of our investigations of the pressure dependence of the photochemical electron-transfer and triplet-sensitized-induced dimerization of CHD.

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