Cykloaddition Eth. + Btdn.
(Diels-Alder)

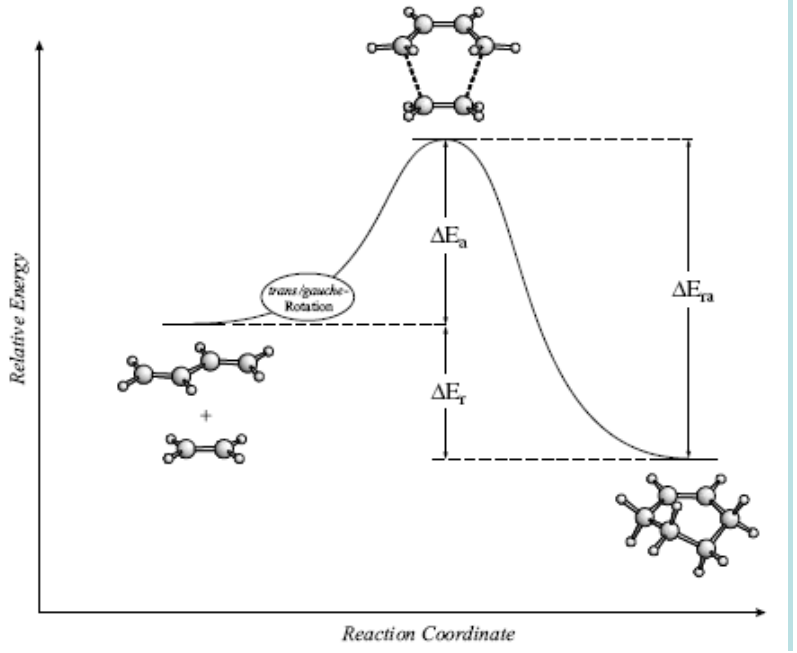

Table 13-2. Computed activation (ΔE_a) and reaction energies (ΔE_r) for the concerted gas-phase cycloaddition of ethylene to *trans*-butadiene [kcal/mol]. The HF and DFT calculations were performed with the 6-311+G(d,p) basis set and include zero-point vibrational contributions.

	Exp.[a]	G2	HF	SVWN	SLYP	BVWN	BLYP	B3LYP
ΔE_a	27 ± 2	25	51	5	–2	33	26	28
ΔE_r	–38	–38	–30	–59	–67	–14	–22	–29

[a] Taken from references cited in Wiest, 1998.

	6-31G(d)	6-31+G(d)	6-31++G(d,p)	6-311++G(3d,2p)	cc-pVTZ
ΔE_a	25	27	27	28	28
ΔE_r	–37	–33	–32	–29	–28

B3LYP

S_N2 Reaction

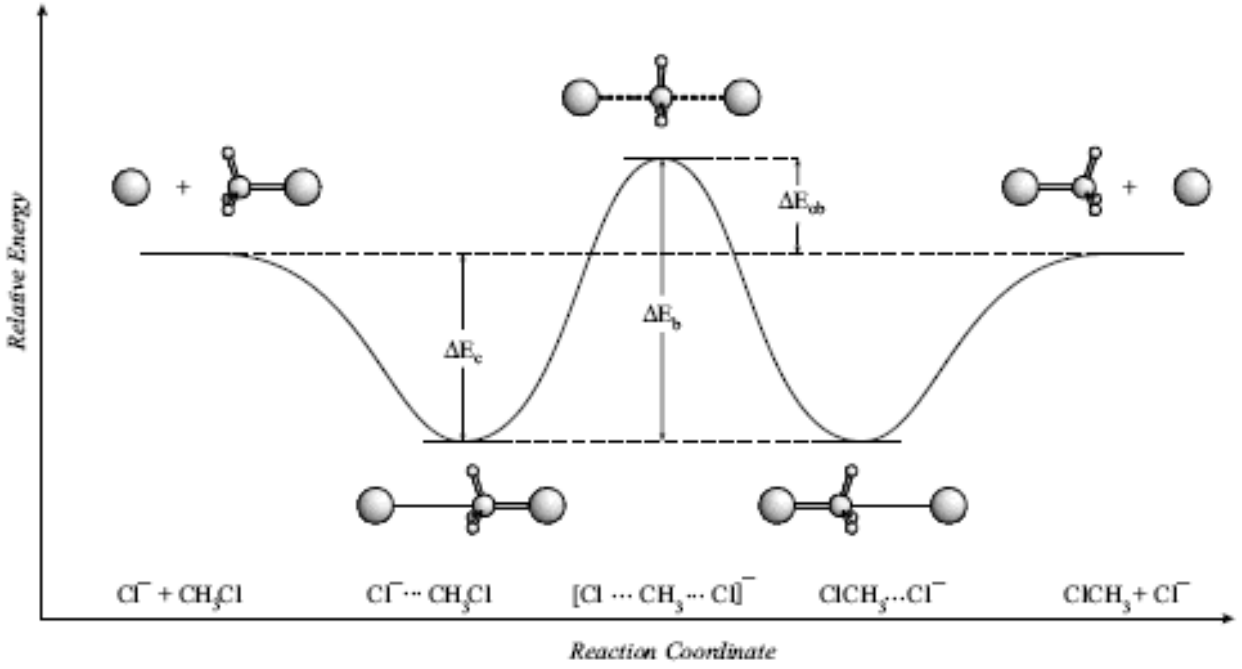

Table 13.4 Complexation energy (ΔE_c) and barrier heights (ΔE_b and ΔE_{ob}, see text) for the gas phase bimolecular S_N2 reaction $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$ at 31

	B3LYP[a]	B3LYP[b]	B1LYP[c]	PBE1PBE[b]	LGLYP[c]	LG1LYP[c]
ΔE_c	–9	–9	–10	–10	–12	–11
ΔE_{ob}	–1	–1	–1	1	–1	–2
ΔE_b	8	8	9	10	11	9

	BPW91[d]	B3PW91[d]	*m*PWPW91[d]	*m*PW1PW91[d]	*m*PW3PW91[d]
ΔE_c	–9	–9	–11	–10	–10
ΔE_{ob}	–3	0	–4	0	0
ΔE_b	6	10	6	11	10

the 6-

LYP

-10
–2
8

A Hydrogen Abstraction Reaction

$$H_2 + H \rightarrow [H\ldots H\ldots H]^{\neq} \rightarrow H + H_2$$

Table 13-7. Computed classical barrier heights ΔE [kcal/mol] for the reaction $H_2 + H \rightarrow [H\cdots H\cdots H]^{\neq} \rightarrow H_2 + H$ (6-311++G(,3pd) basis set); data compiled from Johnson et al., 1994, and Csonka and Johnson, 1998.

	HF	MP2	CCSD(T)	SVWN	SLYP	BVWN	BLYP	B3LYP
ΔE	17.6	13.2	9.9	–2.8	–3.5	3.7	2.9	4.1
ΔE_{SIC}[a]	–	–	–	6.6	6.0	13.2	12.6	11.1

[a] Corrected for self-interaction contributions.

Table 13-8. Self-interaction error components for Coulomb and exchange energies ($E_J + E_X$) as well as for the correlation energy (E_C), and the resulting sum for the H atom, the H_2 molecule, and the H_3 transition structure [kcal/mol]. Data taken from Csonka and Johnson, 1998.

Method	H			H_2			H_3		
	$E_J + E_x$	E_C	SIC	$E_J + E_x$	E_C	SIC	$E_J + E_x$	E_C	SIC
BLYP	0.86	0.00	–0.86	0.38	0.00	–0.38	–8.51	0.00	8.51
B3LYP	2.96	–2.62	–0.34	5.20	–5.45	0.24	0.92	–7.93	7.01

Meta GGA functionals (B95, LAP) works better! (7-8 kcal/mol barrier)

Dipole moments for selected molecules [in D, 1 D = 0.3934 a.u.]

Molecule	HF POL[a]	MP2 POL[a]	SVWN numerical[b]	SVWN TZVP-FIP[c]	BLYP TZVP-FIP[c]	BLYP POL[a]	BLYP 6-31G(d)[d]	B3LYP cc-pVTZ	B3LYP POL[a]	Exp.
CO	-0.25	0.31	0.23	0.24	0.19	0.19	0.15	0.13	0.10	0.11
H_2O	1.98	1.85	1.86	1.88	1.83	1.80	2.04	1.92	1.86	1.85
H_2S	1.11	1.03		1.15	1.07	0.97		1.19	1.01	0.97
HF	1.92	1.80	1.80	1.81	1.76	1.75	1.81	1.83	1.80	1.83
HCl	1.21	1.14				1.08		1.21	1.12	1.11
NH_3	1.62	1.52	1.53	1.57	1.52	1.48	1.90	1.59	1.52	1.47
PH_3	0.71	0.62				0.59		0.53	0.62	0.57
SO_2	1.99	1.54				1.57		2.01	1.67	1.63

[a] taken from Cohen and Tantirungrotechai, 1999;[b] taken from Dickson and Becke, 1996 [c] taken from Calaminici, Jug and Köster, 1998,[d] taken from Johnson, Gill and Pople, 1993

Barrier heights of $H_2 + H \rightarrow H + H_2$ [in kcal/mol]

Method	barrier without SIC	barrier with SIC
LSD	-2.3	5.7
BLYP	2.9	12.6
BPW91	4.7	14.3
B3LYP	4.1	11.1
exp.	**9.7**	

Taken from Johnson, 1995 and Csonka and Johnson, 1998

Compilation of mean absolute deviations for bond lengths [Å] / bond angles [degrees] for small main group molecules from different sources.

32 first row species, 6-31G(d) basis set, Johnson, Gill, and Pople, 1993			
HF	0.020 / 2.0	SVWN	0.021 / 1.9
MP2	0.014 / 1.8	BLYP	0.020 / 2.3
QCISD	0.013 / 1.8		
13 species, Martin, El-Yazal, and François, 1995a			
CCSD(T)/cc-pVDZ	0.018 / 2.2	B3LYP/cc-pVDZ	0.009 / 1.7
CCSD(T)/cc-pVTZ	0.014 / 0.6	B3LYP/cc-pVTZ	0.004 / 0.3
CCSD(T)/cc-pVQZ	0.002 / 0.4	B3LYP/cc-pVQZ	0.004 / 0.3
40 species cont. third row elements, 6-31G(d) basis set, Redfern, Blaudeau and Curtiss, 1997			
MP2	0.022 / 0.4	B3LYP	0.030 / 0.5
BLYP	0.048 / 1.0	B3PW91	0.020 / 0.5
BPW91	0.020 / 0.5		

[a] uncontracted aug-cc-pVTZ basis

Deviations between computed atomization energies and experiment for the JGP test set employing the 6-31G(d) basis set [in kcal/mol]. Taken from Johnson, Gill and Pople, 1993.

	HF	MP2	QCISD	SVWN	SLYP	BVWN	BLYP
mean abs. dev.[a]	86	22	29	36 (40)[a]	38	4 (4)[a]	6
mean dev.	-86	-22	-29	36 (40)[a]	38	0 (4)[a]	1

[a] Basis set free results taken from Becke, 1992.