Gas-Phase Reactions between Diborane and Carbon Monoxide: A Theoretical Study

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Received: June 30, 2003; In Final Form: September 23, 2003

Experimentally, gas-phase reactions between diborane (B_2H_6) and carbon monoxide (CO) produce borane carbonyl (BH_3CO) and a less volatile material. To elucidate the unknown part of the products, we investigated the reactions of the B_2H_6:CO = 1:1 system using ab initio calculations at the MP2/6-311++g** level. Within the energy range of 120 kcal/mol, we located 41 minimum and 35 transition states on the potential energy surface. Among the intermediates and products, BH_2OBHCH_3 is thermodynamically most stable. Its formation releases energy of 64.59 kcal/mol and requires an activation energy of 36.20 kcal/mol at the rate-limiting step. On the contrary, the initially formed $BH_3CO + BH_3$ absorbs 14.75 kcal/mol of energy and requires 19.53 kcal/mol of activation energy. The results indicate that B_2H_6 can act as a reducing agent to hydrogenate CO at thermal equilibrium, whereas the formation of dative complex BH_3CO is kinetically favored. Theoretically, several products containing boron, hydrogen, carbon, and oxygen can be isolated.

I. Introduction

In 1937, Burg and Schlesinger obtained borane carbonyl BH_3CO by heating B_2H_6 in excess CO.[1] When overheated, the yield of BH_3CO decreases whereas an unknown material, heavier and less volatile than BH_3CO, accumulates. As a classical method to prepare BH_3CO and its derivatives,[2−5] the byproduct, so far not well characterized, is undesired. On the other hand, the composition of the byproduct is probably a complicated mixture of several species containing boron, hydrogen, carbon, and oxygen. The pure forms of these species, synthesized in various ways, play important roles in organic synthesis and many related fields.[6−13] If the species produced by direct reactions between B_2H_6 and CO are well-defined and the formation mechanisms toward these products are understood, new synthetic routes, separation methods, and relevant catalysts can be developed. The purpose of the present computational work is, therefore, to elucidate pathways of gas-phase reactions starting from the two molecules B_2H_6 and CO to all stoichiomically possible products. The presumed reactant ratio B_2H_6/CO = 1:1 in this work, though different from that held in Burg and Schlesinger's experiment, is reasonable for theoretical simplicity and may reveal reaction pathways toward useful products which have never been found experimentally.

II. Calculation Method

The geometry structures were fully optimized at the MP2/6-31+G* level. Transition states were located by using synchronous transit-guided quasi-Newton (STQN) methods[14] in combination with stepwise partial optimization along each pathway with one geometric parameter fixed as constant. Frequency calculations were performed following each optimization to obtain the zero point energy (ZPE) and IR spectra data, and to characterize all the stationary points located on the potential energy surface. Intrinsic reaction coordinate (IRC) calculations were performed to confirm the relationship of each transition state with its reactant and product. Single-point calculations at the MP2/6-311++g** level determine the electronic energies. The relative energies finally reported are obtained at this level with MP2/6-31+G* calculated ZPE corrections. The Guassian 98 program package[15] was employed for these calculations.

III. Results and Discussions

Calculated energy, dipole moment, and rotational constants for all the species are listed in Table 1. The kinetic and thermodynamic features for important intermediates and isolable products were summarized in Table 2 and their IR frequencies were given in Table 3. All the species were named according to their structures and numbered to indicate their order of occurrence in the reaction course. Reaction pathways were divided into eleven parts. Each part includes geometry structures of the relevant species and their relative energies (Figures 1−11).

Part I: Formation of BH_3HBH_2CO (3), BH_3CO (4), and $BH_2CH_2OBH_2$ (7) (Figure 1). At the initial stage, B_2H_6 and CO are weakly bonded as shown by molecular complex B_2H_6-CO (**1**). By providing 19.53 kcal/mol of energy, the system is activated to transition state BH_3HBH_2CO (**TS-2**), which leads to formation of BH_3HBH_2CO (**3**). This process usually happens when B_2H_6 is attacked by a Lewis base.[16−18] Upon bonding with CO, B_2H_6 breaks one of its hydrogen-bridged bonds B−H−B and polarizes the other. Thus, the species **3** can be regarded as a complex formed between BH_3CO (**4**) and borane (BH_3), which dissociates with an additional 5.06 kcal/mol of energy. The separated BH_3 can also associate with **4** through a weak O−B bond into BH_3COBH_3 (**5**). The dative complex **4** is the main product of Burg and Schlesinger's experiment.[1] They demonstrated that the formation of **4** requires elevated temperature as well as large amount of CO. The excess CO can combine without barrier to the transient product BH_3 and increases the yield of **4**. Otherwise, the more stable species **3** is likely to exist. For either product, the rate-limiting step is from **1** to **3**. It should be noted that the system requires much less energy to form transition state **TS-2** than to dissociate B_2H_6 to two BH_3 (36.12 kcal/mol), the formation of **4** is thus likely to proceed along the route

$$\mathbf{1} \rightarrow \mathbf{TS\text{-}2} \rightarrow \mathbf{3} \rightarrow \mathbf{4} + BH_3$$

instead of

$$B_2H_6 + CO \rightarrow 2BH_3 + CO \rightarrow BH_3CO + BH_3$$

10.1021/jp035875p CCC: $25.00

TABLE 1: Electronic Energies, Dipole Moments, and Rotational Constants of the Species

species	symm^a	$E_e{}^b$ (au)	$E_e{}^c$ (au)	ZPE^b (kcal/mol)	dipole^b	dipole (D)^c	rotational constants^b (GHZ)		
B_2H_6CO (**1**)	C_1(0)	−166.02736	−166.20886	44.32	0.303	0.372	16.94	1.709	1.598
BH_3HBH_2CO (**TS-2**)	C_1(1)	−165.99241	−166.17731	44.05	4.019	4.027	30.72	2.652	2.548
BH_3HBH_2CO (**3**)	C_s(0)	−166.00883	−166.19373	44.24	3.108	3.104	12.69	4.938	3.780
BH_3CO (**4**)	C_{3v}(0)	−139.53256	−139.66718	23.43	2.057	2.102	122.1	8.505	8.505
BH_3COBH_3 (**5**)	C_1(0)	−166.00048	−166.18081	41.20	1.792	1.827	48.08	2.242	2.221
BH_3COBH_3 (**TS-6**)	C_1(1)	−165.96487	−166.14912	43.03	2.117	2.118	18.74	5.439	4.540
$BH_2CH_2OBH_2$ (**7**)	C_1(0)	−166.05699	−166.23412	47.34	1.813	1.757	18.66	5.378	4.673
B_2H_5CHO (**TS-8**)	C_1(1)	−165.96376	−166.15029	43.72	1.646	1.606	23.94	3.828	3.465
B_2H_5CHO (**9**)	C_1(0)	−166.02179	−166.20078	47.42	2.697	2.581	19.38	4.377	3.918
BH_2HBH_2CHO (**TS-10**)	C_1(1)	−165.97374	−166.15269	45.72	1.975	1.931	11.40	6.600	4.531
c_$BH_2HBH_2CH{-}O$ (**11**)	C_s(0)	−166.02708	−166.20790	47.21	2.094	2.066	12.33	8.944	5.681
BH_2HBH_2CHO (**TS-12**)	C_1(1)	−165.97538	−166.15531	45.59	3.081	2.940	16.25	5.136	4.583
c_BH_2HBH_2CHO (**13**)	C_s(0)	−165.99901	−166.17865	47.04	2.158	2.021	13.97	6.567	5.521
$BH_2HBHCHOH$ (**TS-14**)	C_1(1)	−165.94783	−166.13490	44.39	2.911	2.911	15.44	6.187	4.691
$BH_2HBHCHOH$ (**15**)	C_1(0)	−165.98933	−166.17492	47.98	1.157	1.170	15.51	5.969	4.785
$BH_2CH_2OBH_2$ (**TS-16**)	C_1(1)	−166.00837	−166.19137	46.00	1.609	1.577	13.59	8.915	5.864
$BHHBH_2CH_2O$ (**TS-17**)	C_1(1)	−166.05152	−166.23101	47.85	1.028	0.953	13.74	7.647	5.375
c_$BHHBH_2CH_2O$ (**18**)	C_1(0)	−166.05370	−166.23535	48.86	0.673	1.449	12.80	9.320	5.901
c_BHH_2BHCH_2O (**TS-19**)	C_1(1)	−166.05356	−166.23555	48.75	0.662	0.640	12.65	9.940	6.090
c_BHH_2BHCH_2O (**20**)	C_s(0)	−166.05904	−166.24173	49.66	1.455	1.370	12.50	11.10	6.388
$BH_2CH_2OBH_2$ (**TS-21**)	C_1(1)	−166.05045	−166.22703	47.51	1.787	1.715	19.74	5.089	4.860
c_$BH_2CH_2OBH_2$ (**22**)	C_1(0)	−166.05147	−166.22795	47.84	1.616	1.543	16.30	6.102	5.435
c_BH_2HBHCH_2O (**TS-23**)	C_1(1)	−166.04809	−166.22664	48.25	1.436	1.389	14.69	8.264	6.899
c_BH_2HBHCH_2O (**24**)	C_1(0)	−166.05287	−166.23191	49.46	1.604	1.541	15.35	8.628	7.502
BH_2OBHCH_3 (**TS-25**)	C_1(1)	−165.97963	−166.15963	45.17	4.296	4.174	16.70	6.137	6.007
BH_2OBHCH_3 (**26**)	C_s(0)	−166.13981	−166.31786	48.13	0.752	0.697	38.92	4.063	3.763
BH_2OBHCH_3 (**TS-27**)	C_1(1)	−166.13783	−166.31511	47.86	0.702	0.668	35.99	3.971	3.804
BH_2OBHCH_3 (**28**)	C_1(0)	−166.13947	−166.31472	48.22	0.607	0.593	30.43	4.080	3.801
$BHCH_2OBH_3$ (**TS-29**)	C_1(1)	−166.01151	−166.18856	46.52	4.236	4.169	17.13	5.949	5.030
$BHCH_2OBH_3$ (**30**)	C_1(0)	−166.01285	−166.18972	46.82	4.418	4.345	17.58	5.978	4.972
c_$BHCH_2O$ (**31**)	C_s(0)	−139.53095	−139.66123	26.85	1.556	1.435	31.23	21.47	13.90
c_BH_3HBCH_2O (**32**)	C_1(0)	−165.99865	−166.17534	44.99	1.510	1.390	17.07	3.103	2.847
$BHCH_2OBH_3$ (**TS-33**)	C_1(1)	−165.99846	−166.17651	45.51	1.589	1.486	17.98	3.682	3.342
c_$BH_2H_2BCH_2O$ (**34**)	C_s(0)	−166.03160	−166.21240	49.05	1.761	1.636	21.25	5.371	4.573
c_BH_2HBCH_2OH (**TS-35**)	C_1(1)	−165.94304	−166.12965	46.70	1.022	0.975	11.50	11.17	6.228
c_$BHHBCH_2(OH)$ (**36**)	C_1(0)	−165.98668	−166.17305	49.20	3.527	3.425	11.72	10.65	6.026
c_BH_2BHCH_2OH (**TS-37**)	C_1(1)	−165.97982	−166.16653	48.16	4.321	4.203	11.80	10.86	6.036
c_$BH_2BHCH_2(OH)_c$ (**38**)	C_1(0)	−165.98868	−166.17515	49.14	4.004	3.873	11.74	10.76	6.059
c_$BH_2BHCH_2(OH)_c$ (**TS-39**)	C_1(1)	−165.98525	−166.17097	47.94	3.679	3.572	11.36	10.56	5.965
BH_2BHCH_2OH (**40**)	C_1(0)	−165.99043	−166.17410	47.82	3.476	3.379	10.91	9.864	5.678
c_$BH_2BHCH_2(OH)c$ (**TS-41**)	C_1(1)	−165.98977	−166.173214	47.14	2.804	2.684	11.29	8.489	5.270
BH_2BHCH_2OH (**42**)	C_s(0)	−165.99306	−166.17663	46.93	2.218	2.076	13.50	5.604	4.201
BH_2BHOCH_3 (**TS-43**)	C_1(1)	−165.96138	−166.14862	46.72	1.661	1.590	12.12	10.26	6.031
BH_2BHOCH_3 (**44**)	C_s(0)	−166.04541	−166.22263	48.22	1.838	1.791	15.37	5.491	4.298
$BHOBH_2CH_3$ (**TS-45**)	C_1(1)	−165.95480	−166.13250	47.15	1.768	1.693	14.34	7.065	5.116
$BHOBH_2CH_3$ (**46**)	C_s(0)	−166.09003	−166.27011	46.45	3.954	3.904	21.50	3.352	3.029
BH_2CH_3 (**47**)	C_{2v}(0)	−65.65177	−65.74525	35.95	0.567	0.545	95.93	21.41	19.58
OBH (**48**)	$C_{\infty h}$(0)	−100.43209	−100.51827	9.014	2.735	2.638	0.000	38.30	38.30
BH_2BHOCH_3 (**TS-49**)	C_1(1)	−166.02154	−166.19804	47.32	1.636	1.575	21.07	4.346	3.988
BH_2BHOCH_3 (**50**)	C_s(0)	−166.04765	−166.22468	48.33	1.799	1.734	37.50	3.826	3.656
c_BH_2CH_2BHOH (**TS-51**)	C_1(1)	−165.97130	−166.15669	47.41	3.479	3.372	12.45	9.176	5.669
$B(OH)HCH_2BH_2$ (**52**)	C_1(0)	−166.09762	−166.28236	48.32	1.672	1.574	18.38	4.586	4.344
c_$BH_2H(OH)BCH_2$ (**TS-53**)	C_1(1)	−165.99065	−166.17826	46.76	1.351	1.305	10.53	6.852	4.368
c_$BH_2H(OH)BCH_2$ (**54**)	C_1(0)	−166.03152	−166.21917	48.90	2.440	2.429	20.85	5.347	4.473
$B(OH)HH_2BCH_2$ (**TS-55**)	C_1(1)	−166.02305	−166.21218	47.40	2.721	2.626	20.94	4.008	3.528
$B(OH)HH_2BCH_2$ (**56**)	C_s(0)	−166.03167	−166.22157	48.44	2.661	2.562	34.97	3.317	3.171
$B(OH)HH_2BCH_2$ (**TS-57**)	C_1(1)	−165.98512	−166.17470	45.64	2.604	2.472	8.921	7.890	4.253
$BH_2B(OH)tCH_3$ (**58**)	C_s(0)	−166.07822	−166.26303	48.04	1.974	1.849	8.727	7.219	4.188
c_$CH_3BHHBOH$ (**TS-59**)	C_1(1)	−165.97740	−166.16956	48.62	2.035	1.977	16.72	6.003	4.606
$CH_3BHBH(OH)_t$ (**60**)	C_1(0)	−166.07812	−166.26316	48.54	1.287	1.204	20.98	3.701	3.482

Relative to **1**, the energy is 9.42 kcal/mol for **3** and 14.75 kcal/mol for **4** + BH_3. Thus, thermodynamically, it is more stable for the system to go back to **1** unless CO is in excess as can be seen by the equilibriums

$$B_2H_6 + CO = BH_3CO + BH_3 \qquad \Delta E = 14.17 \text{ kcal/mol}$$

$$B_2H_6 + 2CO = 2BH_3CO \qquad \Delta E = -7.78 \text{ kcal/mol}$$

This result is consistent with the observation that BH_3CO decomposes readily to CO and B_2H_6, and the decomposition is suppressed by an excess of CO.

If the temperature is higher, vibration in **5** can activate the system to transition state BH_3COBH_3 (**TS-6**). By providing 36.20 kcal/mol of energy to the system, oxygen can coordinate to boron and carbon can be reduced by abstracting two hydrogen atoms from each boron atom. The product is $BH_2CH_2OBH_2$ (**7**) with an energy of −12.83 kcal/mol relative to **1**. Although the energy to reach the transition state **TS-6** is sufficient to dissociate B_2H_6 into two BH_3 fragments, the formation of **TS-6** is more likely to happen since the system is thermodynamically favored to form carbon-reduced product **7**. As we can see in

TABLE 1: (Continued)

species	symm[a]	E_e[b] (au)	E_e[c] (au)	ZPE[b] (kcal/mol)	dipole[b]	dipole (D)[c]	rotational constants[b] (GHZ)		
$CH_3BHBH(OH)_t$ (**TS-61**)	$C_1(1)$	−166.01315	−166.20215	46.73	2.300	2.155	32.81	3.651	3.334
BHH(O)BCH$_3$ (**TS-62**)	$C_1(1)$	−166.11967	−166.30085	48.12	1.879	1.811	27.01	4.774	4.317
BH$_2$H(O)BCH$_3$ (**63**)	$C_s(0)$	−166.12063	−166.30215	48.96	2.771	2.675	23.97	5.012	4.417
BH$_3$OBCH$_3$ (**TS-64**)	$C_1(1)$	−166.09823	−166.27932	46.93	5.199	5.147	19.40	4.142	3.595
BH$_3$OBCH$_3$ (**65**)	$C_3(0)$	−166.10284	−166.28191	47.61	7.008	6.948	68.47	3.018	3.018
OBCH$_3$ (**66**)	$C_{3v}(0)$	−139.62184	−139.75490	27.69	3.625	3.513	159.4	7.817	7.817
c_BHOBCH$_3$H$_2$ (**TS-67**)	$C_1(1)$	−166.03202	−166.21778	46.93	2.166	2.061	19.86	5.317	5.014
c_BHOBCH3H$_2$ (**68**)	$C_1(0)$	−166.06604	−166.24446	42.85	1.079	1.010	17.98	4.466	3.660
c_BHOBCH$_3$ (**69**)	$C_s(0)$	−164.92116	−165.08333	35.53	0.984	0.913	30.13	5.694	4.935
c_BHOBCH$_3$ (**TS-70**)	$C_1(1)$	−165.97047	−166.15700	45.99	0.600	0.526	34.59	3.568	3.308
BH$_2$BHCH$_2$OH (**TS-71**)	$C_1(1)$	−165.98238	−166.16590	46.84	2.206	2.042	15.65	4.799	4.185
c_BH$_2$BHCH$_2$OH (**72**)	$C_1(0)$	−165.98756	−166.17099	47.88	2.829	2.709	15.73	5.528	4.958
BH$_2$HBHCHOH (**TS-73**)	$C_1(1)$	−165.95303	−166.13940	46.28	4.239	4.273	17.53	5.002	4.267
c_BH$_2$HBHCHOH (**74**)	$C_1(0)$	−165.99794	−166.18319	48.12	0.921	0.888	17.36	5.542	4.915
BH$_2$CH(OH)BH$_2$ (**TS-75**)	$C_1(1)$	−165.98773	−166.17295	46.02	1.477	1.359	13.81	6.789	5.339
BH$_2$CH(OH)BH$_2$ (**76**)	$C_1(0)$	−166.00127	−166.18564	46.08	1.811	1.685	9.352	8.368	4.825
H_2	$D_{\infty h}(0)$	−1.14414	−1.16030	6.48	0.000	0.000	0.000	1842	1842
CO	$C_{\infty h}$ (0)	−113.02865	−113.11477	3.02	0.196	0.255	0.000	55.61	55.61
BH_3	$D_{3h}(0)$	−26.46635	−26.51198	17.00	0.000	0.000	235.5	235.5	117.7
B_2H_6	$D_{2h}(0)$	−52.99703	−53.09251	40.90	0.000	0.000	80.66	18.52	17.00

[a] Symmetry of the species, the number of imaginary frequency is in parentheses. [b] MP2/6-31+G*// MP2/6-31+G* calculations. [c] MP2/6-311++G**// MP2/6-31+G* calculations.

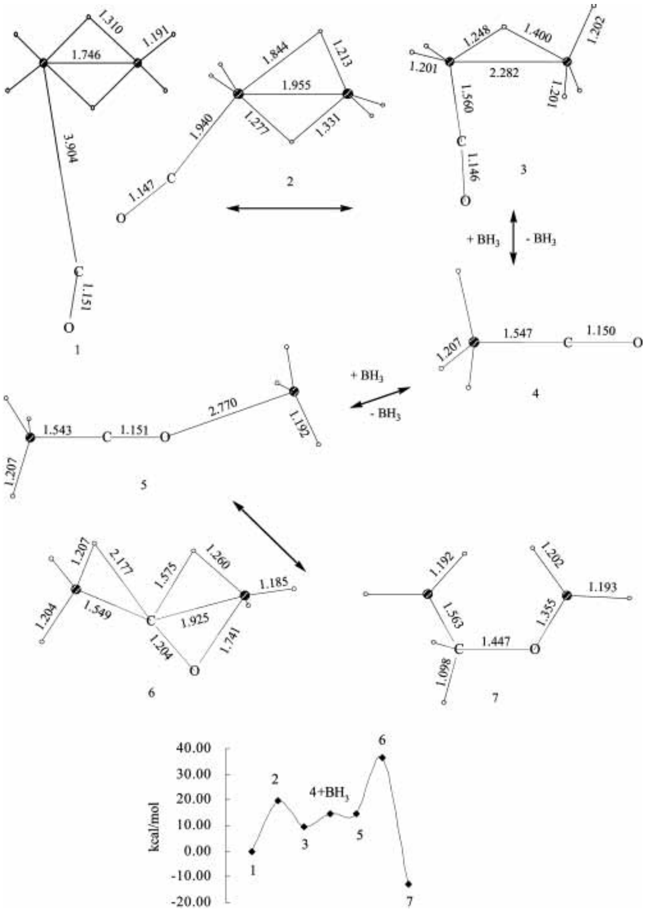

Figure 1. Species involved in forming BH$_3$HBH$_2$CO (**3**), BH$_3$CO (**4**), and BH$_2$CH$_2$OBH$_2$ (**7**); bond lengths are in Å; the species on or under the double arows are transition states or BH3. The relative energy of B$_2$H$_6$CO (**1**) is 0.00 kcal/mol.

Part III, however, compound **7** may only be an intermediate that cannot be isolated due to rapid further reactions.

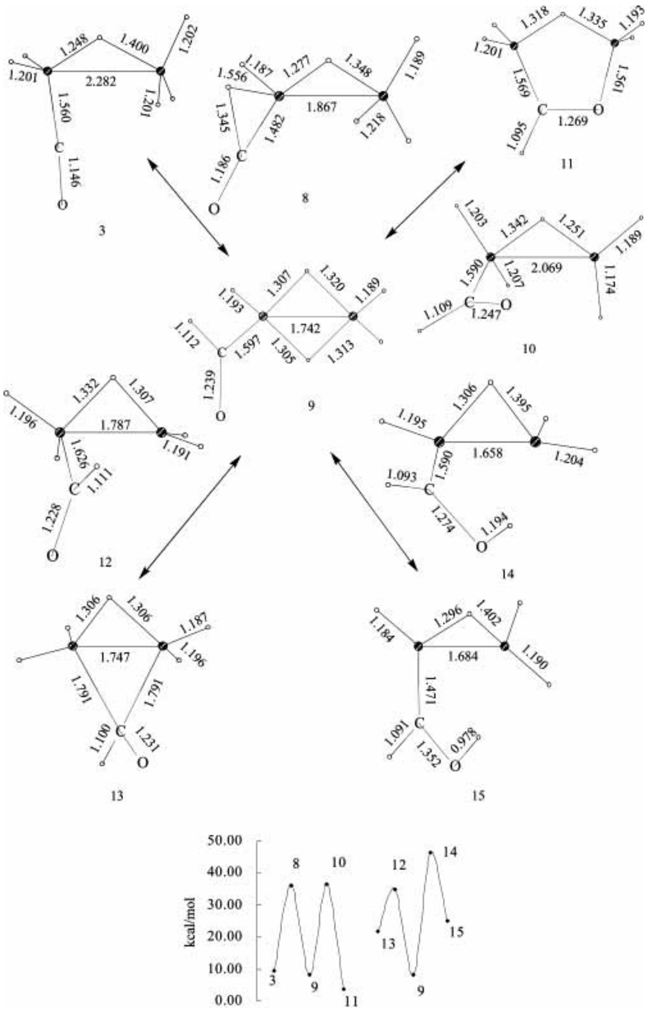

Figure 2. Species involved in forming B$_2$H$_5$CHO (**9**), c_BH$_2$HBH$_2$-CH−O (**11**), c_BH$_2$HBH$_2$CHO (**13**), and BH$_2$HBHCHOH (**15**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B$_2$H$_6$CO (**1**) is 0.00 kcal/mol.

Part II: Formation of B$_2$H$_5$CHO (9), c_BH$_2$HBH$_2$CH−O (11), c_BH$_2$HBH$_2$CHO (13), and BH$_2$HBHCHOH (15) (Figure 2). In compound **7**, carbon is double-hydrogenated. Starting from **3**, carbon can also be monohydrogenated. By providing 36.15 kcal/mol of energy to the system, the carbon atom in **3** abstracts one hydrogen atom from boron while the double B−H−B bond remains or rebuilds as shown by transition state B$_2$H$_5$CHO (**TS-8**) and product B$_2$H$_5$CHO (**9**). Isolation of the

TABLE 2: Kinetic and Equilibrium Energies for Reactions between B_2H_6 and CO[a]

reactions	ΔE_a[b]	ΔE_e[c]	reaction steps[d]
B_2H_6+CO→			
B_2H_6CO (**1**)		−0.58	
BH_3HBH_2CO (**3**)	19.53	9.42	**1** → **TS-2** → **3**
BH_3CO (**4**) + BH_3	19.53	14.75	**1** → **TS-2** → **3** → **4** + BH_3
$BH_2CH_2OBH_2$ (**7**)	36.20	−12.83	**1** → **3** → **4** + BH_3 → **5** → **TS-6** → **7**
B_2H_5CHO (**9**)	36.15	8.17	**1** → **3** → **TS-8** → **9**
c_BH_2HBH_2CH−O (**11**)	36.65	3.50	**1** → **3** → **9** → **TS-10** → **11**
c_BH_2HBH_2CHO (**13**)	36.15	21.68	**1** → **3** → **TS-8** → **9** → **13**
$BH_2HBHCHOH$ (**15**)	46.48	24.95	**1** → **3** → **9** → **TS-14** → **15**
c_BHH_2BHCH_2O (**20**)	36.20	−15.28	**1** → **3** → **4** + BH_3 → **5** → **TS-6** → **7** → **18** → **20**
BH_2OBHCH_3 (**26**)	36.20	−64.59	**1** → **3** → **4** + BH_3 → **5** → **TS-6** → **7** → **22** → **24** → **26**
$BHCH_2O$ (**31**) + BH_3	36.20	21.90	**1** → **3** → **4** + BH_3 → **5** → **TS-6** → **7** → **22** → **24** → **30** → **31** + BH_3
c_$BH_2H_2BCH_2O$ (**34**)	36.20	2.51	**1** → **3** → **4** + BH_3 → **5** → **TS-6** → **7** → **22** → **24** → **30** → **31** + BH_3 → **32** → **34**
BH_2BHCH_2OH (**42**)	46.48	22.84	**1** → **3** → **9** → **TS-14** → **15** → **42**
BH_2CH_3 (**47**) + OBH (**48**)	50.75	−33.65	**1** → **3** → **4** + BH_3 → **5** → **7** → **18** → **20** → **44** → **TS-45** → **46** → **47** + **48**
BH_2BHOCH_3 (**50**)	40.20	−5.91	**1** → **3** → **4** + BH_3 → **5** → **7** → **18** → **20** → **TS-43** → **44** → **50**
B(OH)HCH_2BH_2 (**52**)	46.48	−42.12	**1** → **3** → **9** → **TS-14** → **15** → **42** → **40** → **38** → **52**
c_BH_2H(OH)BCH_2 (**54**)	46.48	−1.89	**1** → **3** → **9** → **TS-14** → **15** → **42** → **40** → **38** → **52** → **54**
BH(OH)H_2BCH_2 (**56**)	46.48	−3.85	**1** → **3** → **9** → **TS-14** → **15** → **42** → **40** → **38** → **52** → **56**
BH_2B(OH)CH_3 (**58**)	46.48	−30.27	**1** → **3** → **9** → **TS-14** → **15** → **42** → **40** → **38** → **52** → **58**
BH(OH)$BHCH_3$ (**60**)	46.48	−29.85	**1** → **3** → **9** → **TS-14** → **15** → **42** → **40** → **38** → **52** → **60**
$OBCH_3$ (**66**) + BH_3	36.20	−36.03	**1** → **3** → **4** + BH_3 → **5** → **TS-6** → **7** → **22** → **24** → **26** → **63** → **65** → **66** + BH_3
c_$BHOBCH_3$ (**69**) + H_2	36.20	−24.12	**1** → **3** → **4** + BH_3 → **5** → **TS-6** → **7** → **22** → **24** → **26** → **68** → **69** + H_2
$BH_2CHOHBH_2$ (**76**)	46.48	16.33	**1** → **3** → **9** → **TS-14** → **15** → **74** → **76**

[a] Calculation at the MP2/6-311++G**//MP2/6-31+G*+ZPE level. See relevant figures for the geometry structures and detailed steps for each reaction. [b] The highest activation energy (kcal/mol) or the energy required to activate the rate-limiting step. [c] The energy difference (kcal/mol) between reactants and products. [d] The transition states listed are those with highest energies in the steps.

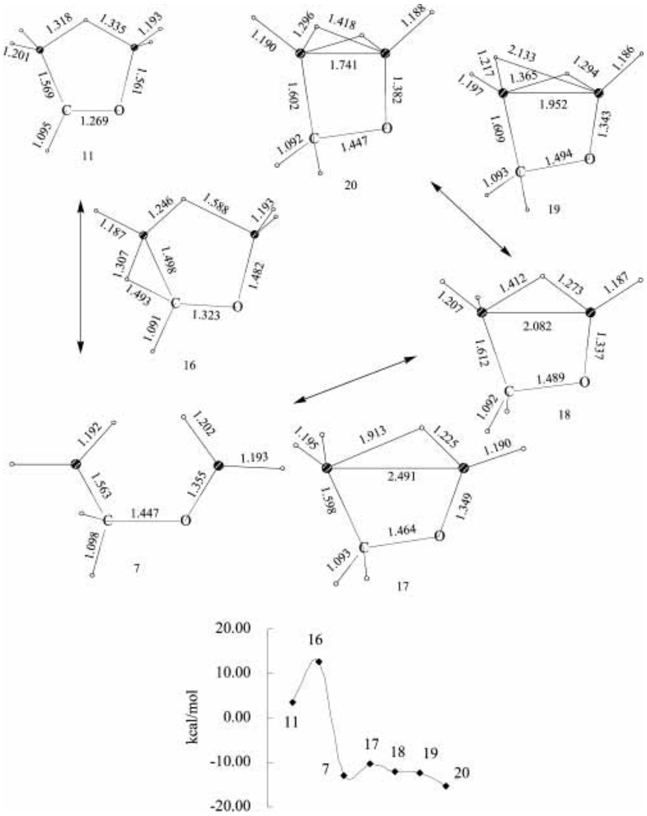

Figure 3. Species involved in forming c_BHH_2BHCH_2O (**20**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B_2H_6CO (**1**) is 0.00 kcal/mol.

B_2H_6-like compound **9** is probably feasible if the heating condition is carefully controlled. Otherwise, the system may not stop at **9** but proceed to the more stable c_BH_2HBH_2CH−O (**11**). From **9** to **11**, one of the B−H−B bonds breaks, and a five-member ring forms as shown by transition state BH_2HBH_2-CH−O (**TS-10**). The barrier of the process is 28.48 kcal/mol relative to **9**. Compared to **1**, the species **9** and **11** are 8.17 and 3.50 kcal/mol less stable, but both are more stable than **3**.

Over a barrier of 26.70 kcal/mol, species **9** can transform to another less stable isomer c_BH_2HBH_2CHO (**13**). The energy of **13** is 13.51 kcal/mol relative to **9**. As shown by transition state BH_2HBH_2CHO (**TS-12**), carbon coordinates both boron atoms, leading to a four-member ring with a carbon bridge replacing one of the hydrogen bridges in B_2H_6. Consequently, unlike the usual aldehyde, the carbon in **13** is four coordinated. The formation and relative stability of **9** and **13** imply that either a terminal or a bridge hydrogen atom in B_2H_6 can be substituted by a −CHO group, but the former process is more likely to happen and results in a more stable product.

Over a larger barrier of 38.31 kcal/mol, one of the bridging hydrogen atoms in **9** can transfer to oxygen via transition state $BH_2HBHCHOH$ (**TS-14**), forming an alcohol-like species BH_2-HBHCHOH (**15**). Interestingly, unlike the usual alcohol, the carbon bonded to the OH group in **15** is three coordinated. Relative to **9**, the energy of **15** is 16.78 kcal/mol. The unusual carbon bonding type in **13** and **15** may account for their relative higher energies compared to **9**.

Part III: Formation of c_BHH_2BHCH_2O (20) (Figure 3). The three-coordinated carbon in **11** has a tendency to attract a second hydrogen atom from boron as shown by the transition state $BH_2CH_2OBH_2$ (**TS-16**). Accompanying the change, the −H− in B−H−B moves to one boron and **7** forms. The barrier from **11** to **7** is 9.17 kcal/mol relative to **11**. The two boron atoms are separated in **7** only tentatively, over a small barrier (2.46 kcal/mol) they associate again by forming a B−H−B bond into ring structure c_$BHHBH_2CH_2O$ (**18**), which then rearranges almost without barrier into c_BHH_2BHCH_2O (**20**) with a double

TABLE 3: Calculated Vibrational Frequency and IR Intensity of the Species Produced by Reaction between B_2H_6 and CO [a]

B_2H_6CO (**1**)	377 (15), 1013 (21), 1235 (74), 1806 (498), 2114 (42), 2675 (154), 2785 (199)
BH_3HBH_2CO (**3**)	508 (54), 1007 (124), 1145 (147), 1168 (10), 1567 (94), 2186 (168), 2319 (198), 2571 (20), 2606 (28), 2669 (57), 2670 (98), 2677 (112)
BH_3CO (**4**)	715 (39), 2147 (296), 2623 (55)
$BH_2CH_2OBH_2$ (**7**)	772 (24), 1054 (67), 1065 (56), 1100 (32), 1240 (29), 1274 (36), 1369 (73), 1419 (191), 1494 (46), 2623 (119), 2675 (79), 2742 (202), 2767 (110), 3067 (28)
B_2H_5CHO (**9**)	308 (20), 542 (13), 1185 (24), 1234 (37), 1437 (8), 1690 (64), 1784 (542), 2693 (91), 2710 (38), 2797 (79), 2948 (128)
c_BH_2HBH_2CHO (**11**)	749 (41), 828 (26), 952 (15), 1021 (143), 1094 (18), 1096 (6), 1220 (81), 1416 (34), 1630 (68), 1713 (20), 2164 (659), 2602 (38), 2660 (89), 2667 (70), 757 (123), 3170 (29)
c_BH_2HBH_2CHO (**13**)	469 (13), 631 (18), 984 (14), 1019 (13), 1072 (24), 1217 (64), 1639 (76), 1917 (163), 2149 (26), 2656 (98), 2787 (108), 3081 (52)
$BH_2HBHCHOH$ (**15**)	168 (24), 300 (16), 594 (89), 647 (23), 765 (13), 891 (22), 905 (65), 939 (21), 993 (26), 1074 (24), 1128 (105), 1233 (59), 1252 (116), 1368 (37), 1460 (121), 1544 (145), 2139 (81), 2667 (96), 2765 (40), 2777 (87), 3686 (57)
c_BHH_2BHCH_2O (**20**)	376 (12), 784 (39), 866 (21), 902 (16), 1054 (92), 1080 (11), 1159 (124), 1298 (73), 1334 (34), 1510 (209), 1526 (16), 2144 (25), 2238 (44), 2744 (95), 2767 (102), 3136 (17), 3204 (11)
BH_2OBHCH_3 (**26**)	1028 (44), 1065 (10), 1084 (78), 1106 (82), 1331 (55), 1364 (485), 1412 (422), 1507 (8), 1513 (18), 2648 (74), 2670 (187), 2759 (186), 3199 (12)
c_$BHCH_2O$ (**31**)	666 (36), 875 (22), 959 (26), 1026 (66), 1227 (15), 1388 (48), 1548 (15), 2828 (79), 3189 (8)
c_$BH_2H_2BCH_2O$ (**34**)	561 (22), 636 (19), 781 (54), 1031 (66), 1204 (22), 1213 (28), 1413 (91), 1551 (19), 1734 (544), 2209 (10), 2293 (15), 2688 (60), 2791 (67), 3179 (11)
BH_2BHCH_2OH (**42**)	125 (27), 315 (116), 349 (23), 469 (19), 656 (13), 837 (14), 992 (23), 1074 (31), 1156 (79), 1216 (34), 1264 (10), 1500 (19), 2642 (91), 2657 (57), 2717 (99), 3028 (39), 3071 (23), 3740 (30)
BH_2CH_3 (**47**)	993 (11), 1103 (20), 1127 (72), 1299 (28), 1391 (80), 2653 (114), 2729 (171), 3152 (12), 3203 (13)
OBH (**48**)	768 (12), 1802 (34)
BH_2BHOCH_3 (**50**)	575 (10), 778 (23), 956 (14), 983 (37), 1018 (38), 1150 (15), 1220 (58), 1261 (17), 1403 (281), 1557 (12), 2574 (162), 2646 (63), 2713 (123), 3103 (50), 3205 (21), 3215 (18)
B (OH)HCH_2BH_2 (**52**)	622 (132), 879 (32), 940 (73), 1071 (56), 1083 (54), 1134 (125), 1149 (45), 1210 (95), 1299 (116), 1385 (289), 1492 (20), 2645 (146), 2658 (144), 2728 (160), 3186 (5), 3762 (90)
c_BH_2H (OH)BCH_2 (**54**)	473 (22), 566 (12), 690 (17), 733 (92), 782 (14), 820 (39), 890 (115), 1001 (49), 1006 (50), 1052 (48), 1123 (76), 1243 (88), 1588 (51), 1878 (343), 2185 (62), 2680 (94), 2789 (97), 3724 (185)
BH (OH)H_2BCH_2 (**56**)	375 (116), 720 (128), 775 (73), 838 (10), 985 (23), 1026 (58), 1133 (205), 1278 (347), 1399 (58), 1553 (58), 1680 (17), 1688 (369), 2361 (35), 2710 (102), 3794 (102)
BH_2B (OH)CH_3 (**58**)	371 (13), 596 (68), 731 (61), 834 (7), 943 (20), 979 (61), 981 (104), 1205 (74), 1261 (96), 1342 (93), 1397 (85), 1506 (10), 2644 (70), 2710 (122), 3068 (8), 3154 (25), 3717 (35)
BH (OH)$BHCH_3$ (**60**)	613 (49), 720 (16), 845 (59), 910 (111), 966 (49), 1032 (18), 1180 (68), 1198 (126), 1372 (72), 1390 (59), 2591 (183), 2632 (129), 3144 (17), 3192 (16), 3751 (74)
$OBCH_3$ (**66**)	356 (12), 948 (24), 1398 (20), 1509 (10), 1986 (133)
c_$BHOBCH_3$ (**69**)	918 (20), 1026 (99), 1175 (81), 1365 (16), 1490 (74), 1507 (41), 1516 (22), 2804 (83)
BH_2CH (OH)BH_2 (**76**)	237 (74), 298 (58), 383 (12), 695 (15), 770 (28), 836 (11), 900 (37), 1048 (19), 1080 (69), 1118 (95), 1160 (29), 1262 (57), 1267 (52)

[a] TheMP2/6-31+G* calculated frequencies (cm^{-1}, not scaled) with intensities (in parentheses) larger than 10 km/mol.

B−H−B bond. The energy drops only 2.45 kcal/mol from **7** to **20**. The transition state $BHHBH_2CH_2O$ (**TS-17**) lies about 2 kcal/mol higher in energy than **7** and **18**. The energy of c_BHH_2BHCH_2O (**TS-19**) is very close to that of **18**. As we will show in later parts, intermediates **7** and **20** are both subject to further reactions. Since the energy difference and barriers between **7**, **18**, and **20** are small, their mutual transformation is rapid. As a result, the species are conformers but not separable isomers.

Part IV: Formation of c_BH_2OBHCH_3 (26) (Figure 4). Compound **7** can undergo another change into a three-member-ring structure c_$BH_2CH_2OBH_2$ (**22**), because the oxygen is attracted by boron as shown by transition state c_$BH_2CH_2OBH_2$ (**TS-21**). The barrier is small (4.62 kcal/mol). The two boron atoms in **21** are then hydrogen bridged to form c_BH_2HBHCH_2O (**24**) over a barrier of 5.60 kcal/mol, as shown by transition state c_BH_2HBHCH_2O (**TS-23**). Relative to **7**, the energies are 4.37 kcal/mol for **22** and 3.51 kcal/mol for **24**. The energy change of the rearrangement from **7** to **24** is so small that no intermediate species involved can be isolated.

In **24**, oxygen not only bridges two boron atoms but also bonds to carbon, showing its strong electron-donating character. By providing 31.75 kcal/mol of energy, the carbon can switch from oxygen bridge to hydrogen bridge as shown by transition state BH_2OBHCH_3 (**TS-25**). The system becomes much more stable as a hydrogen atom transfers from B−H−B to carbon, leading to formation of BH_2OBHCH_3 (**26**). The energy of **26** is −64.59 kcal/mol relative to **1**. Ether-like **26** is the most stable isomer for the total system. Oxygen serves as a strong electron donor bridging two electron-deficient boron atoms and carbon is also satisfied in the four-coordinated $-CH_3$ group. This accounts for its stability. The B−O bond rotates essentially free to transform **26** to its slightly less stable conformer BH_2OBHCH_3 (**28**) (2.06 kcal/mol relative to **26**). The barrier is only 1.45 kcal/mol as shown by transition state BH_2OBHCH_3 (**TS-27**).

Part V: Formation of c_$BHCH_2OH$ (31) and c_$BH_2H_2CH_2O$ (34) (Figure 5). The hydrogen-bridge bond B−H−B in **24** is a point to break with a BH_3 group eliminated. Over a barrier of 24.26 kcal/mol, as shown by transition state c_$BHCH_2OBH_3$ (**TS-29**), BH_3 is partially eliminated to form the intermediate c_$BHCH_2OBH_3$ (**30**). The full BH_3 elimination can take place with 7.39 kcal/mol more energy. The total energy required for the process is 31.21 kcal/mol, lower than 36.12 kcal/mol, the dissociation energy of B_2H_6. The product c_$BHCH_2O$ (**31**) can be regarded as a BH_3 derivative with two hydrogen atoms replaced by a $-CH_2O-$ group forming a ring structure. Also, it is a boron-substituted epoxy ethane, an attractive species that may be applicable in asymmetric synthesis.[19] BH_3 and **31** can be weakly bonded as c_BH_3HBCH_2O (**32**), which then associate almost without barrier into another

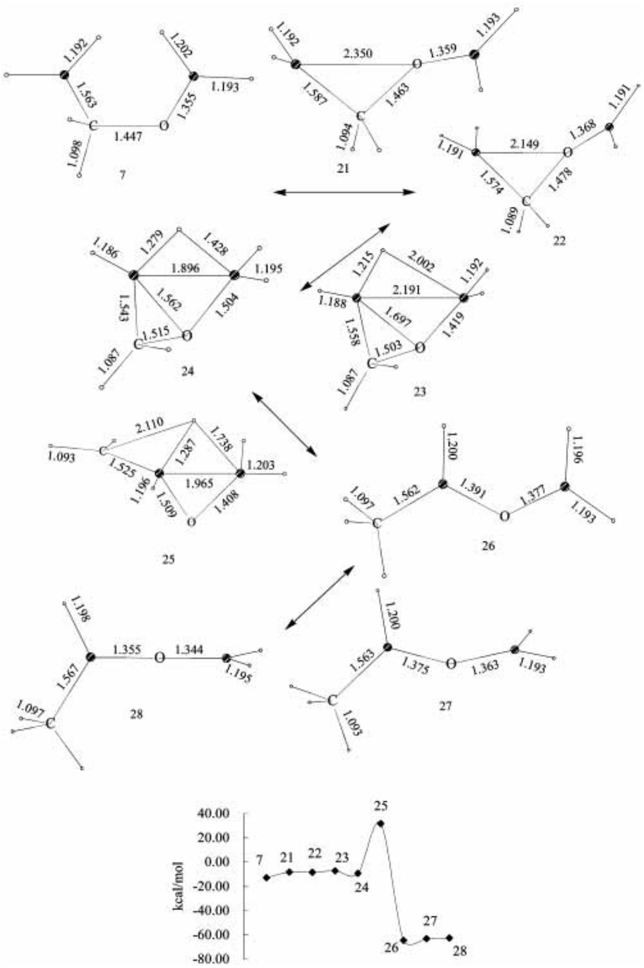

Figure 4. Species involved in forming BH_2OBHCH_3 (**26**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B_2H_6CO (**1**) is 0.00 kcal/mol.

B_2H_6-like structure c_$BH_2H_2BCH_2O$ (**34**); the energy of **34** falls to 2.51 kcal/mol relative to **1**. The transient existence of intermediate c_$BH_3H{-}BCH_2O$ (**32**) and transition state c_BH_3-$HBCH_2O$ (**TS-33**) indicates that **31** is a little more stable than BH_3, because there is no evidence that two BH_3 can coexist by such a loose complex. Therefore, besides the more stable **34**, compound **31** is also a possible isolable product if BH_3 is consumed or removed in some way.

It looks like a more compact transition state should mediate **24** and **34** directly. However, such a state was not found. BH_3 dissociating followed by recombination seems the only pathway from **24** to **34**.

Part VI: Formation of c_$BH_2BHCH_2(OH)_c$ (38), c_BH_2-$BHCH_2OH$ (40), and BH_2BHCH_2OH (42) (Figure 6). The H in the B−H−B bond is partially positive charged due to bonding with two-electron-deficient boron. It is thus feasible for it to migrate to an electron-rich atom such as oxygen. The process can be realized as the double ring species **20** is activated to the transition state c_$BHHBHCH_2OH$ (**TS-35**). Its formation requires 52.09 kcal/mol of energy relative to **1**, the most energy demanding process considered in this work. The direct product of the hydrogen transfer is c_$BHHBHCH_2(OH)_t$ (**36**), a ring species containing a B−H−B bond and an OH group. The energy of **36** is 27.35 kcal/mol relative to **1**. The H in the OH group is trans to the remaining B−H−B bond. Compound **36** can transform to its cis conformer c_$BHHBHCH_2(OH)_c$ (**38**), 1.37 kcal/mol more stable, overcoming a small barrier of 3.05 kcal/mol through transition state c_$BHHBHCH_2OH$ (**TS-37**).

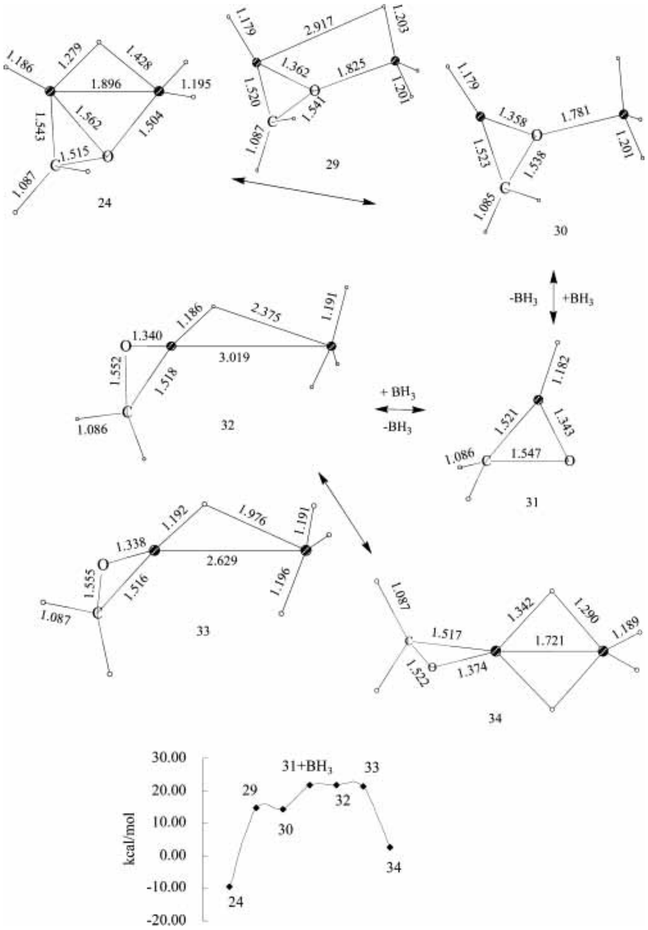

Figure 5. Species involved in forming c_$BHCH_2O$ (**31**) and c_BH_2H_2-BCH_2O (**34**); bond lengths are in Å; the species on or under the double arrows are transition states or BH_3. The relative energy of B_2H_6CO (**1**) is 0.00 kcal/mol.

The double-ring structure of **38** is quite easy to disrupt. First, the B−H−B bond breaks through transition state BH_2BHCH_2-OH (**TS-39**), resulting in a four-member-ring structure c_BH_2-$BHCH_2OH$ (**40**). The weak O−B bond in **40** then breaks with a very small barrier as shown by transition state c_BH_2BHCH_2-OH (**TS-41**), resulting in BH_2BHCH_2OH (**42**). Consequently, the isomerization from the double-ring **38** to the single-ring **40** to the chain structure **42**, although involving bond breaking, encounters almost no barriers. The potential energy surface is so flat along the line from **36** to **42** that the species involved interconvert from each other rapidly and cannot be isolated. Starting from **20**, the H transfer from boron to oxygen is quite difficult. As we will show in Part XI, compound **42** can be produced more easily from **15**.

Part VII: Formation of BH_2CH_3(47), OBH(48), and BH_2BHOCH_{3c}(50) (Figure 7). By providing 40.20 kcal/mol of energy to the system, a hydrogen atom transfers from boron to carbon while the C−B bond breaks as shown by transition state structure c_BH_2BHOCH_3 (**TS-43**). The barrier for this transfer is 11.89 kcal/mol lower than that encountered from **20** to **36**, indicating in such a case that the −H− is easier to transfer to carbon than to oxygen. The formation of the methyl group in BH_2BHOCH_3 (**44)** marks the complete reduction of carbon. Relative to **1**, the energy of **44** is −4.74 kcal/mol. In the most stable isomer **26**, oxygen coordinates to both boron atoms, whereas in **44**, oxygen bonds to boron and carbon, leaving another electron-deficient boron as the active part. Consequently, the energy of **44** is much higher than that of **26**. Compound **44** converts to a slightly more stable cis conformer BH_2BHOCH_{3c}

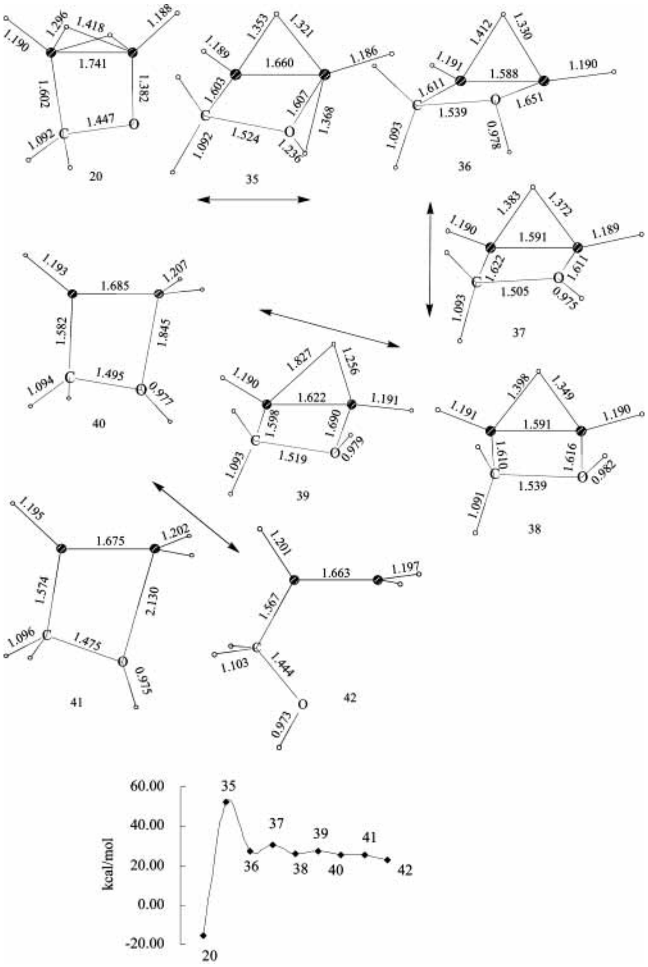

Figure 6. Species involved in forming c_$BH_2BHCH_2(OH)_c$ (**38**), c_BH_2BHCH_2OH (**40**), and BH_2BHCH_2OH (**42**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B_2H_6CO (**1**) is 0.00 kcal/mol.

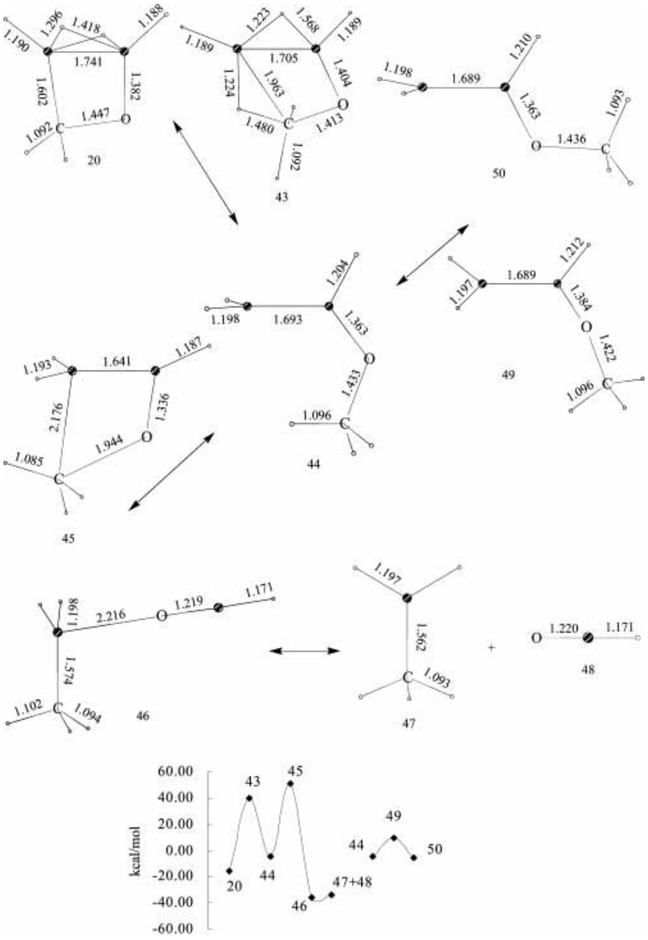

Figure 7. Species involved in forming BH_2CH_3 (**47**), OBH (**48**), and $BH_2BHO(CH_3)_c$ (**50**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B_2H_6CO (**1**) is 0.00 kcal/mol.

(**50**) over a rotational barrier of 14.53 kcal/mol. The transition state is BH_2BHOCH_3 (**TS-49**). The energy of **50** is −5.91 kcal/mol relative to **1**. Compounds **44** or **50** are probably isolable.

Over a barrier of 55.49 kcal/mol of energy relative to **44**, the methyl group attached to oxygen in **44** can migrate to another boron as shown by transition state BH_2BHOCH_3 (**TS-45**). This migration results in the break of the B−B bond and the formation of $HBOBH_2CH_3$ (**46**), which is a donor−acceptor complex formed between OBH (**48**) and BH_2CH_3 (**47**). Despite the large barrier for the process, the products are quite stable. The energy of **46** is −36.30 kcal/mol relative to **1** and 2.65 kcal/mol more energy is needed to dissociate **46** into **48** and **47**. It is remarkable that the monomethyl-substituted borane **47** can be produced by direct reaction of B_2H_6 with CO. Another interesting product **48** has been studied as an isoelectronic species of CO.[20,21] Because **48** coordinates to **47** in a similar way as CO coordinates to BH_3, the existence of **46** is a theoretical example supporting such an analogy. However, the donating atom is oxygen in **46** and the interaction is considerably weaker than that in **4**.

Part VIII: Formation of BH(OH)CH_2BH_2 (52), BH_2H(OH)BCH_2 (54), and BH(OH)H_2CH_2 (56) (Figure 8). The ring structure of compound **38** plays an important role in intramolecular rearrangement. Since the OH group is not stable as a bridge, bond breaking may take place in two possible ways. The O−B bond breaking results in the formation of **42** as described in Part VI. From **38** to **42**, the system's energy drops only slightly. Over a barrier of 8.48 kcal/mol, the C−O bond breaks and a C−B forms as shown by transition state c_BH_2CH_2BHOH (**TS-51**). The ring disrupts and a more stable species BH_2CH_2BHOH (**52**) forms. From **38** to **52**, the energy drops to −42.12 kcal/mol relative to **1**. Examining the structures of **38** and **52**, perhaps the stronger coordination effect of the $-CH_2-$ group accounts for the relative stability of the latter. The two boron atoms in **52**, being three coordinated, attract each other and have the potential to form a B−H−B bond. Starting from **52**, there are four routes leading to different products. First, as the B−H−B bond forms, −OH replaces $-CH_2-$ to become a bridge, as shown by transition state c_$BH_2H(OH)BCH_2$ (**TS-53**) and product c_$BH_2H(OH)BCH_2$ (**54**). The energy of **54** is 40.23 kcal/mol relative to **52** and the activation energy from **52** to **54** is 63.76 kcal/mol. Compound **54** is a B_2H_6-like species. Its energy is −1.89 kcal/mol relative to **1**, quite close to the B_2H_6 plus CO. The formation and relative stability of **54** implies that the −OH group can act as a bridged hydrogen while one $-CH_2$ group can act as two terminal hydrogen atoms. The second route is similar to the first one albeit with −H− replacing $-CH_2-$ to become a bridge as shown by transition state c_BH(OH)H_2BCH_2 (**TS-55**). The barrier for the process is 43.12 kcal/mol, lower than that encountered in the first route. The product is c_BH(OH)H_2BCH_2 (**56**), another B_2H_6-like species, with energy of −3.85 kcal/mol relative to **1**. IRC calculations show that both replacing processes are mediated by structures with B−H−B and two $-CH_2-$ bridges. Such structures, however, are not stationary points on the potential energy surface. Also,

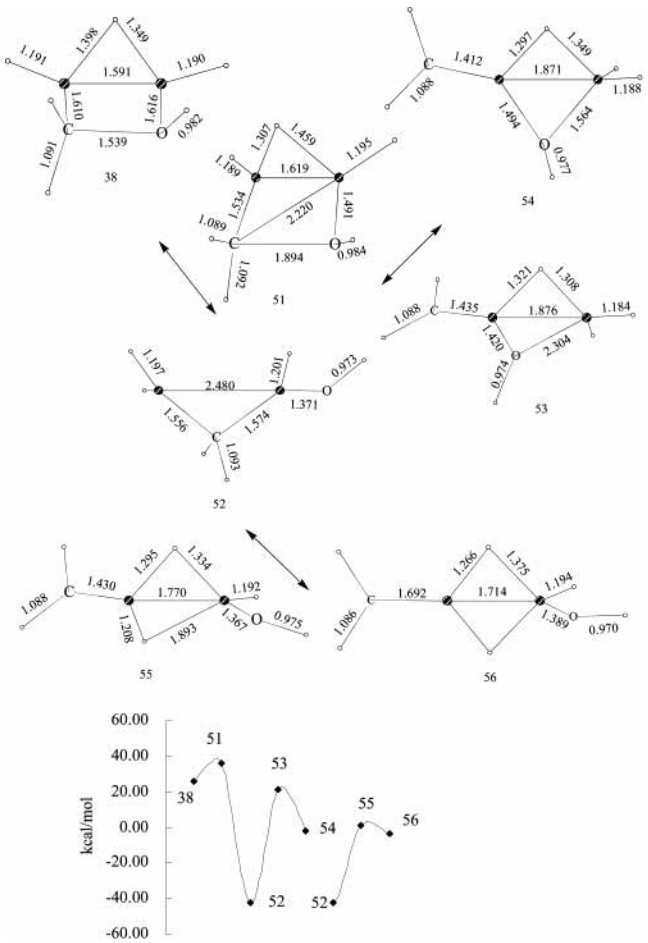

Figure 8. Species involved in forming BH(OH)CH$_2$BH$_2$ (**52**), BH$_2$H(OH)BCH$_2$ (**54**), and BH(OH)H$_2$BCH$_2$ (**56**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B$_2$H$_6$CO (**1**) is 0.00 kcal/mol.

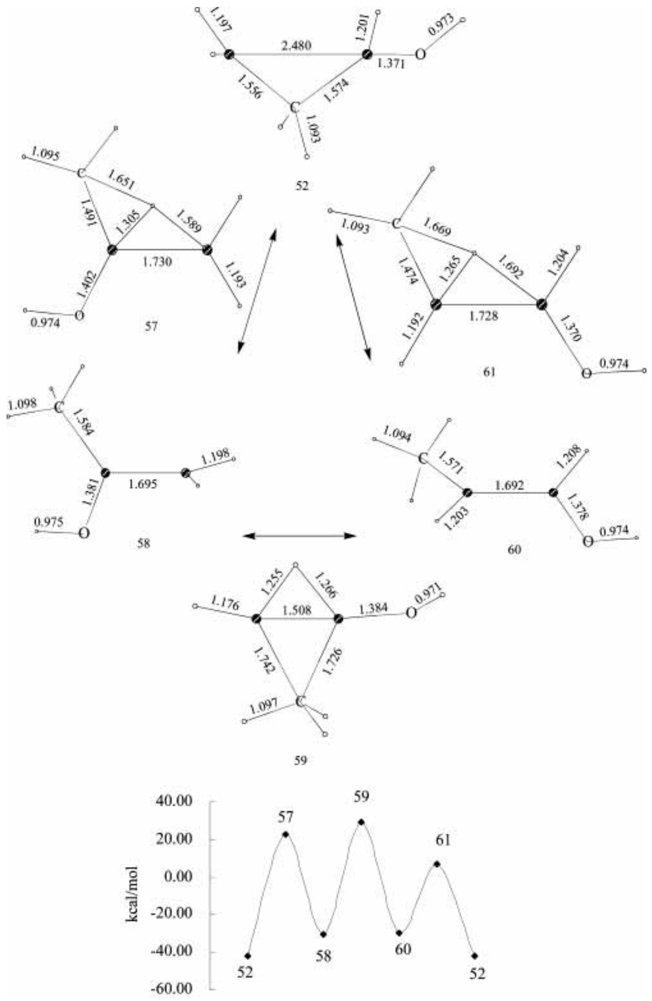

Figure 9. Species involved in forming BH$_2$B(OH)CH$_3$ (**58**) and BH(OH)BHCH$_3$ (**60**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B$_2$H$_6$CO (**1**) is 0.00 kcal/mol.

it should be mentioned that in **52**, **55**, and **56**, the −OH group is cis to the adjacent B−H bond. The corresponding trans species (not shown) exist with similar energies. The interconversion between cis and trans conformers, realizable by rotating a B−O bond, requires 6−13 kcal/mol of energy. Compared with **52**, the ring species **38**, **54**, and **56** are much less stable, and the barriers for them to transfer to **52** are small. Therefore, these species are difficult to isolate. The third and forth routes, involving H transfer from boron to carbon, will be discussed in Part IX.

Part IX: Formation of BH$_2$B(OH)CH$_3$ (58) and BH(OH)BHCH$_3$ (60) (Figure 9). In **52**, there are two types of H atoms bonded to boron. For type I, one H atom and one OH group connect with the same boron. For type II, two H connect with the same boron. Because each of the H atoms is potentially able to transfer to carbon, the transition states and products also are of two types. The transition states contain a H atom bridging three atoms, two borons and one carbon. In transition state BH$_2$B(OH)CH$_3$ (**TS-61**), the bridging H is type I. In transition state BH(OH)BHCH$_3$ (**TS-57**), the bridging H is type II. The products are two types of carbon fully reduced species BH$_2$B(OH)CH$_3$ (**58**) and BH(OH)BHCH$_3$ (**60**). The energies of **58** and **60**, −30.27 and −29.85 kcal/mol relative to **1**, are essentially the same and both are slightly less stable than **52**. But from **52**, it is relatively easier to obtain **60** than **58**, because relative to **52**, the barrier through **TS-57** to **58** is 64.87 kcal/mol whereas the barrier through **TS-61** to **60** is 48.75 kcal/mol.

Besides formation directly from **52**, the two species **58** and **60** can convert to each other by methyl shifting as shown by transition state BHHBOHCH$_3$ (**TS-59**), in which a CH$_3$ group acts as a bridge. The barrier is 59.23 kcal/mol relative to **58**. Because of the stability and the large barriers inhibiting further reactions, compounds **52**, **58**, and **60** are isolable products.

Part X: Formation of OBCH$_3$ (66) and c_BHOBCH$_3$ (69) (Figure 10). Two paths lead to decomposition of the most stable species **26**. Both are energy rising processes, First, by providing energy more than 28.56 kcal/mol, BH$_3$ can be eliminated in a stepwise manner. The two separated boron atoms in **26** associate into a four-coordinated ring structure BH$_2$H(O)BCH$_3$ (**63**) that requires 10.67 kcal/mol energy to reach the transition state BH$_2$H(O)BCH$_3$ (**TS-62**). With additional energy of 12.29 kcal/mol, BH$_3$ can be eliminated as shown by the transition state BH$_3$OBCH$_3$ (**TS-64**) and the product BH$_3$OBCH$_3$ (**65**), which is a complex formed between OBCH$_3$ (**66**) and BH$_3$, an analogue structure of **46**. The BH$_3$ in **65** connects more closely to its electron donor **66**, a methyl derivative of OBH (**48**). The full BH$_3$ elimination takes place when 6.52 kcal/mol more energy is provided. The linear structure of the O−B−CH$_3$(H) bond in **66** and **48** shows some multiple bonding characteristics, which have been recently documented.[22−24] The energy of **65** is −36.03 kcal/mol relative to **1**, quite stable for the total system. If the transient product BH$_3$ is consumed, it may be easy for the ether-like species **26** to decompose by modest heating.

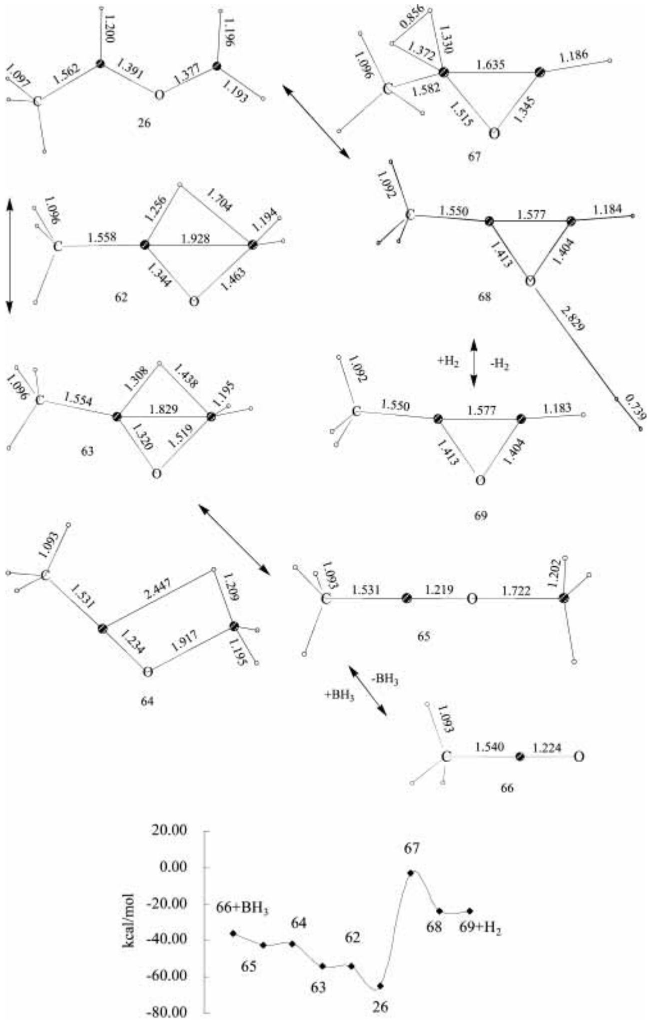

Figure 10. Species involved in forming $OBCH_3$ (**66**) and c_$BHOBCH_3$ (**69**); bond lengths are in Å; the species on or under the double arrows are transition states, BH_3, or H_2. The relative energy of B_2H_6CO (**1**) is 0.00 kcal/mol.

The second probable fate of **26** is H_2 elimination, as shown by transition state c_$BHO(H_2)BCH_3$ (**TS-67**), the association of two hydrogen atoms from each boron resulting in the formation of a H−H bond. Compared with the first process, the second one is energy demanding. It requires 61.60 kcal/mol of energy to activate **26** to **67**. However, the energy of the total system is still lower than that of **1**. Thus, compound c_$BHOBCH_3$–H_2 (**68**), or its molecular fragments c_BH−O−B−CH_3 (**69**) and H_2, are also possible decomposition products of **26**. The energy of **68** is −23.81 kcal/mol relative to **1**, indicating **69** is a thermodynamically stable species and isolable. This is another boron-substituted epoxy ethane. The three members constituting the ring are two boron atoms and one oxygen atom.

Part XI: Formation of BH_2BHCH_2OH (42), c_BH_2BHCH_2OH (72), c_$BH_2H(CHOH)BH$ (74), and $BH_2CHOHBH_2$ (76) (Figure 11). Compound **15** produced in Part II has two active points, the B−H−B bond and the monohydrogenated carbon. Over a barrier of 9.26 kcal/mol relative to **15**, the H in B−H−B can transfer to carbon as shown by transition state BH_2BHCH_2OH (**TS-70**), resulting in BH_2BHCH_2OH (**42**). As we have shown in Part VI, the structure of **42** is so flexible that it fluctuates between double-ring (**38**), mono-ring (**40**), and chain (**42**) frequently. Also, over a barrier of 6.64 kcal/mol, the oxygen of the OH group can coordinate with boron through transition state c_BH_2BHCH_2OH (**TS-72**), forming three-member-ring c_BH_2BHCH_2OH (**72**). The energy of **72** is 27.33 kcal/mol relative to **1**. Again, because of the small barrier between **72** and **42**, they are difficult to isolate as distinct species. On the other hand, from **38**, the system can convert readily to the much more stable species **52** as shown in Part VIII. Therefore, species **42** (or **38**, **40**, **72**) is actually a transient intermediate. Its formation is easier from **15** than from **20** (see Part VI).

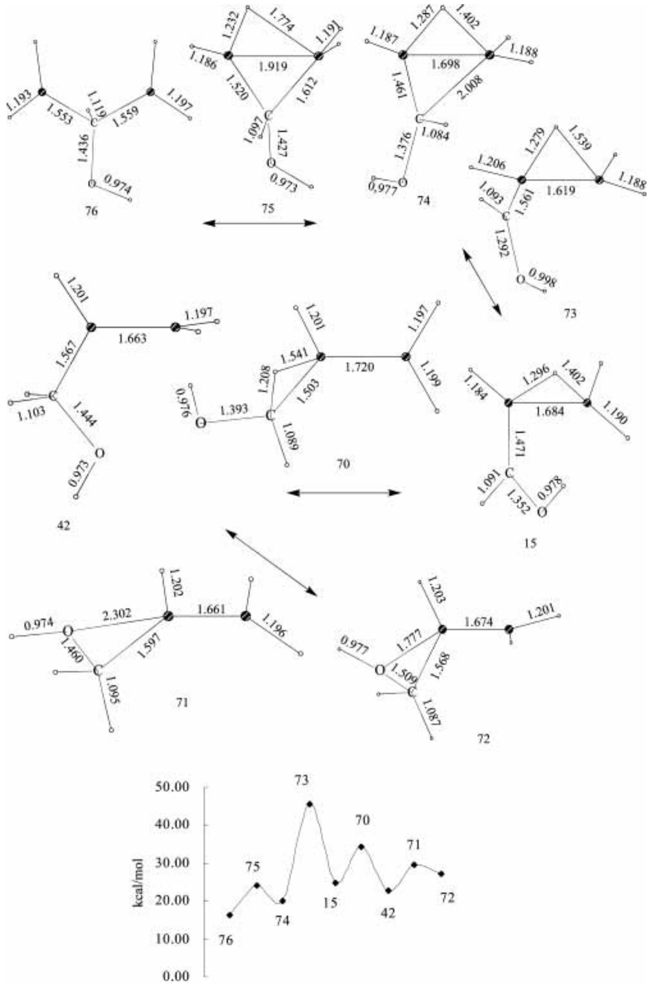

Figure 11. Species involved in forming BH_2BHCH_2OH (**42**), c_BH_2BHCH_2OH (**72**), c_$BH_2H(CHOH)BH$ (**74**), and $BH_2CHOHBH_2$ (**76**); bond lengths are in Å; the species on or under the double arrows are transition states. The relative energy of B_2H_6CO(**1**) is 0.00 kcal/mol.

Being monohydrogenated, the carbon atom in **15** can coordinate with another boron, forming a loose ring structure c_$BH_2HBHCHOH$ (**74**). Although the process is realizable through C−B bond rotation, the barrier through transition state c_$BH_2HBHCHOH$ (**TS-73**) is 20.60 kcal/mol, much larger than the barrier of the usual single bond rotation. Compound **74** is 5.04 kcal/mol more stable than **15** and transfers readily to the slightly more stable (−8.62 kcal/mol relative to **15**) species $BH_2CHOHBH_2$ (**76**). As shown by the structure of transition state $BH_2CHOHBH_2$ (**TS-75**), the product **76** is formed by breaking the B−H−B bond and strengthening the C−B bond. The barrier for the process is 4.33 kcal/mol relative to **74**. Thus, species **76** and **74** may be isolated as mixtures with the production ratio a little favored for **76**.

IV. Concluding Remarks

Among the 41 minima located on the potential energy surface, only those trapped between relative deep energy valleys or fragmented species are isolable. Such potential products and a few crucial intermediates of the reactions between B_2H_6 and CO are summarized in Table 2. Their IR spectral data were listed in Table 3. The number of steps from the initial reactants to each product is different. Among the relative energies of transition states for all the steps, the highest one is approximated as activation energy, since it represents the energy required for the rate-limiting step. It can be seen that the reactants need the smallest activation energy to produce BH_3CO and BH_3, but this is an energy-rising process. By providing higher activation energy, such as heating at higher temperature or for a longer time, the system can reach its thermal equilibrium, several species can be produced, and the system becomes more stable by lowering the total energy. The unknown material obtained in the experiment is probably a mixture of the species predicted in this work. The most stable product is BH_2OBHCH_3 (**26**), its formation releases 64.59 kcal/mol energy. To isolate a particular product is possible through kinetic, thermal, and polarity control as well as appropriate separation methods.

The limitation of this work lies in three aspects. First, the highest energy for the system is assumed lower than 60 kcal/mol; at higher energies, a wide range of reactions would certainly occur. Second, the reactions were considered as interaction between two molecules B_2H_6 and CO, the probable third-body assistance were excluded. Third, the products should be regarded as initial ones, because in a real situation, some of them may react with each other or with other reactants rapidly and result in more complicated products.

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