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Energetics of Aluminum Combustion

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Aluminum continues to be of great interest as a fuel in propellant formulations. Quantitative modeling of the multistep ignition and combustion processes requires considerable thermodynamic and kinetic data, some of which are currently not available or not reliable. We have accordingly carried out CBS-QB3 calculations of the enthalpies and free energies, at 298 and 2000 K, of atoms and molecules that are likely to be involved in the combustion of aluminum-based propellants. These have been used to find the respective heats of formation, as well as the heats of reaction and equilibrium constants for numerous possible steps in the ignition/combustion processes. In a few instances, we also determined transition states and activation barriers. Certain interesting aspects of the results are discussed in greater detail.

I. Introduction

Because of the large negative enthalpies of formation of both liquid and solid Al_2O_3, −387.325 and −400.5 kcal/mol,[1] the oxidation of metallic aluminum to either of these products is accompanied by a heat release of more than 7 kcal/g of aluminum. This potential as an energy source, as well as the ability of aluminum particles to help reduce combustion instability in rocket motors, has led to their frequent use as an ingredient in propellant formulations.[2,3] There is accordingly a continuing effort, through extensive experimental and modeling studies, to develop a better quantitative understanding of the processes involved in aluminum ignition and combustion.[4−15] Considerable thermodynamic and kinetic data are required as input for the modeling (e.g., heats of formation, activation barriers, etc.), some of which are not currently available or are not reliable.[16,17] For example, Belyung et al have quoted heats of reaction with uncertainties of as much as 22 kcal/mol.[14] This can lead to even qualitatively incorrect conclusions; the direction of exothermicity or equilibrium in a reaction step may be predicted incorrectly.

We have therefore undertaken the computational determination, at a relatively high level, of the enthalpies and free energies at 298 and 2000 K of a large number of gas-phase atoms and molecules that have been implicated in the combustion of aluminum-based propellants. (This large number of possible intermediates and products reflects the variety of oxidizers that may be involved, e.g., NH_4ClO_4, nitramines, difluoramines, etc.) The results that have been obtained can be used to find the heats of formation of these species, as well as the heats of reaction, free energy changes, and equilibrium constants for numerous possible steps in the ignition and combustion processes. For a few of these, we have also characterized intermediates and transition states and calculated the activation barriers. The present studies overlap to some extent our earlier ones related to boron ignition/combustion.[18−21]

II. Methods

All computations were carried out with the CBS-QB3 procedure,[22] which involves density functional (B3LYP) geometry optimization and ab initio "complete basis set" extrapolation. The Gaussian 98 code was used.[23] In earlier testing that included 125 dissociation energies, ionization potentials, electron affinities, and proton affinities, the mean absolute CBS-QB3 error was only 0.87 kcal/mol.[22]

For each atom and molecule were found the energy minimum at 0 K (corresponding to the optimized geometry) and the enthalpies and free energies at 298 and 2000 K. Gas phase heats of formation at 298 K were obtained by calculating ΔH for the formation of each species from its elements. For molecules containing carbon or aluminum, which are solids at 298 K, it was necessary to include their experimental heats of sublimation, 171.288 and 78.8 kcal/mol, respectively.[1]

Energy minima were verified by the absence of imaginary vibrational frequencies, and transition states, by the presence of a single one.[24] The intrinsic reaction coordinate technique was used to confirm that these led to the desired products.[25,26]

III. Results and Discussion

A. Structures. Our optimized geometries for the aluminum-containing molecules are shown in Figures 1 and 2. All of these correspond to energy minima. We have found experimental bond lengths for only six: AlH, 1.6482 Å; AlO, 1.6176 Å; AlF, 1.6544 Å; AlCl, 2.1301 Å;[27] AlF_3, 1.631 Å;[28] $AlCl_3$, 2.062 Å.[29] These differ by an average of 0.020 Å from our computed values, which is more than the average discrepancy that we have obtained earlier with the CBS-QB3 procedure for a total of 61 molecules of various types, 0.009 Å.[18,21]

B. Energies, Enthalpies, and Free Energies. In Table 1 are listed the computed (CBS-QB3) energy minima at 0 K and enthalpies and free energies at 298 and 2000 K of 85 gas-phase atoms and molecules. (The aluminum oxides are numbered to correspond to the structures in Figure 1.) The E_{min} do not include zero-point contributions. The data for some of the non-aluminum-containing molecules were presented earlier,[19−21] in relation to boron ignition/combustion. Table 1 contains several sets of isomers; their relative stabilities will be examined in a later section. (This table does not include all possible isomeric aluminum oxides. For other theoretical and experimental studies, that also investigate the anions and excited states, see Nemukhin and Weinhold,[30] Desai et al,[31] and Ghanty and Davidson.[32])

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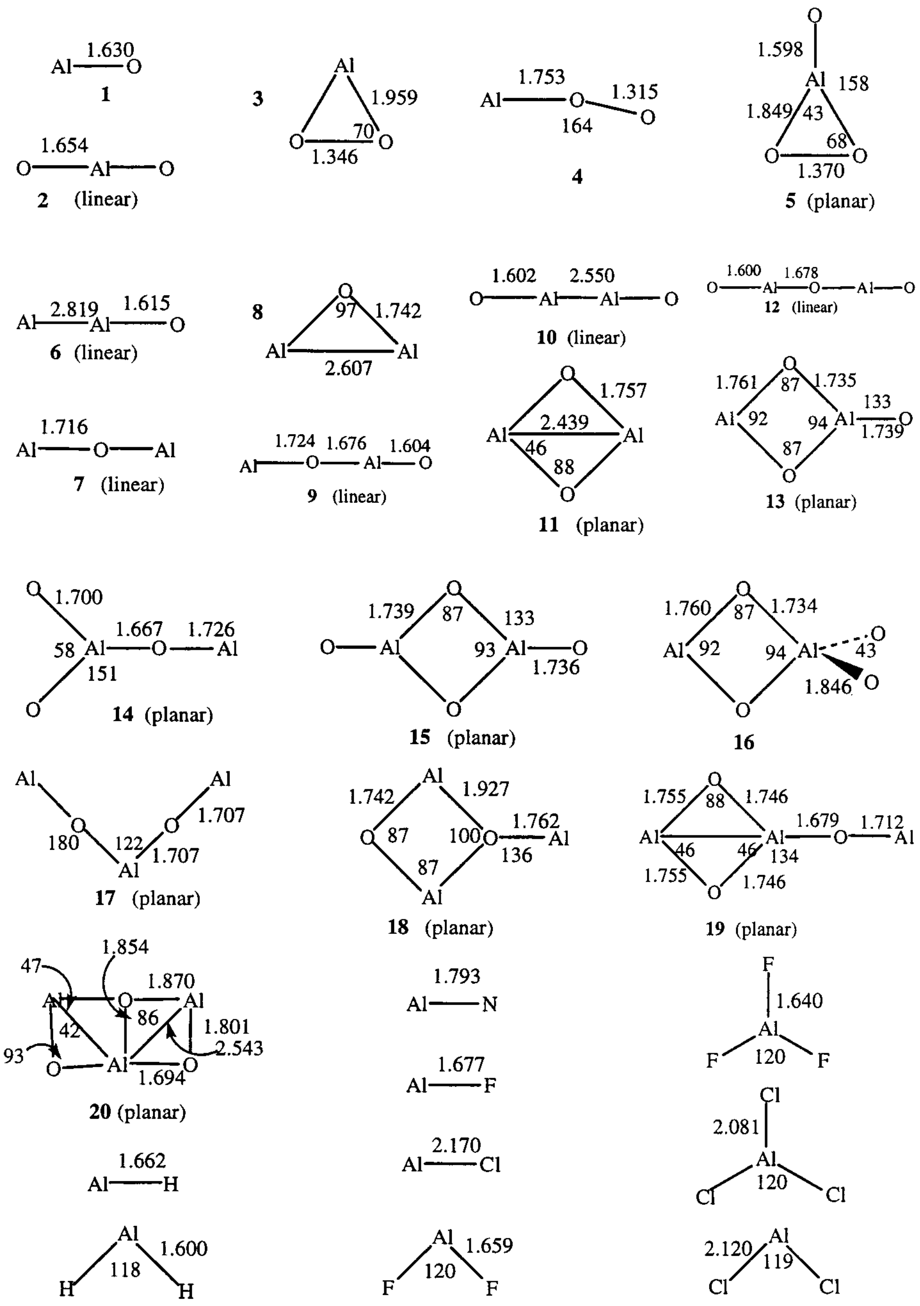

Figure 1. Computed bond lengths (Å) and bond angles (deg) in binary aluminum-containing molecules.

C. Heats of Formation. The enthalpies at 298 K in Table 1 were used to calculate gas phase heats of formation for 78 atoms and molecules. (About one-fourth of these have also been computed, by several different correlated procedures, in a recent analysis of aluminum combustion thermochemistry by Swihart and Catoire.[17]) Our results are given in Table 2 and compared to available experimental values, taken primarily from the NIST compilation.[1] The average absolute difference is 1.6 kcal/mol. In some instances, the NIST experimental heats of formation are not included in Table 2 because other sources[14,17,27,33−37] have indicated that they have substantial levels of uncertainty. This seems to frequently be the case, for example, for the molecules MX_2, where M = B or Al and X = H or a halogen.[18,21,36,38]

D. Heats of Reaction. The enthalpies in Table 1 can be used to determine ΔH at either 298 or 2000 K for numerous possible gas-phase reactions. If it is desired to have aluminum in either the solid or liquid phase, it is only necessary to appropriately include its heat of sublimation (78.8 kcal/mol) or its heat of vaporization (76.3 kcal/mol).[1] ΔH(298 K) can of course also be obtained with the heats of formation in Table 2.

An assessment of temperature effects can be made from the results in Table 3 for a group of 15 representative reactions. The average absolute errors are 1.5 kcal/mol at 298 K and 1.1 kcal/mol at 2000 K. These are quite similar to what we found in our recent CBS-QB3 study of boron ignition/combustion:[21] 1.3 and 1.4 kcal/mol, respectively. The enthalpies of the individual atoms and molecules in Table 1 increase in going from 298 to 2000 K, sometimes quite considerably, e.g., 33.0 kcal/mol in the case of $AlCl_3$. However, the heats of reaction, ΔH, change very little over this temperature range. This has already been pointed out earlier[18,20,21] and is seen again in Table 3. The average absolute difference between the computed ΔH(298 K) and ΔH(2000 K) is 1.9 kcal/mol; for the experimental, it is 1.1 kcal/mol. In only one instance is the predicted

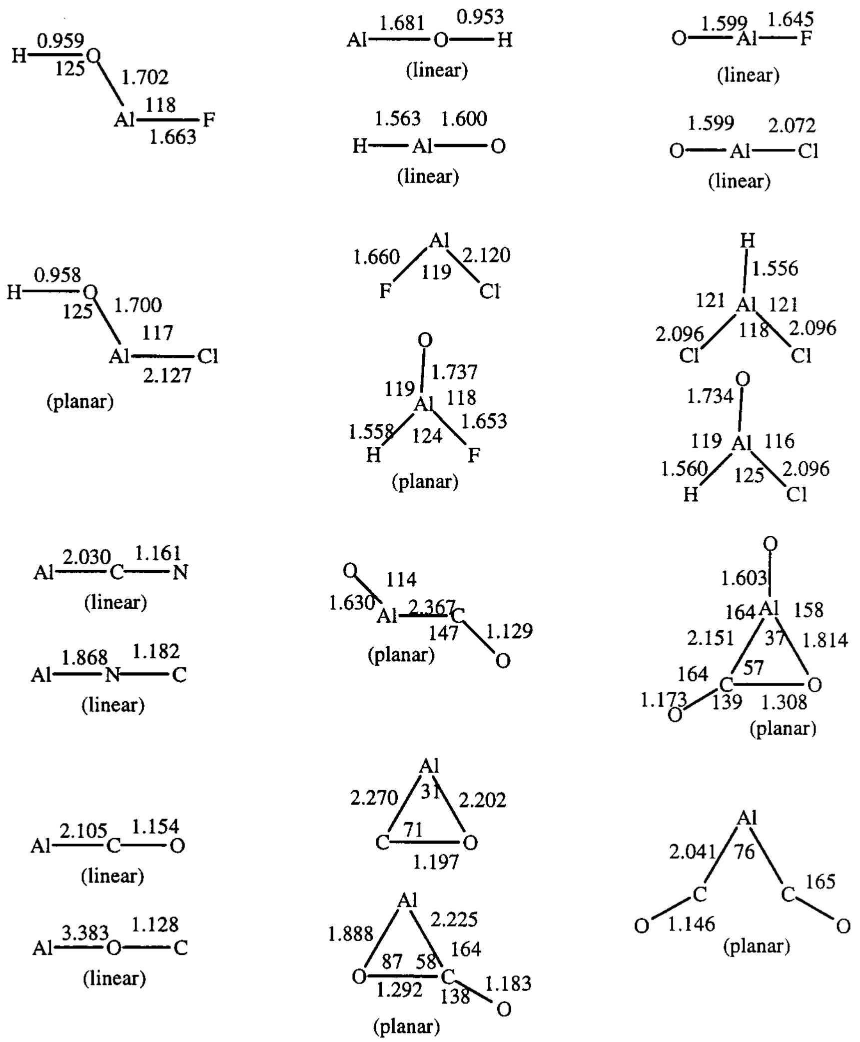

Figure 2. Computed bond lengths (Å) and bond angles (deg) in remaining aluminum-containing molecules.

change in ΔH (increase or decrease) in the opposite direction from that of the observed.

In Table 4 are the calculated ΔH(298 K) for 77 gas-phase reactions that are possible steps in the combustion of aluminum. Experimental values are given when available. The average absolute difference is 1.9 kcal/mol. These computed heats of reaction, together with others that can be determined from the data in Table 2, should provide a firmer foundation for some past analyses and interpretations (see, for instance, Belyung et al.[14]) as well as facilitating others. Some examples will be mentioned.

The $AlO + O_2$ reaction has been studied by Belyung and Fontijn.[9] They concluded that the dominant channel above 1200 K leads to $AlO_2 + O$, whereas the primary pathway below 1000 K yields AlO_3. The latter is not known in the gas phase but is believed to have been obtained in solid matrixes.[39] Our optimized structure for AlO_3 (Figure 1) is in agreement with the qualitative one proposed,[39] and our predicted heat of formation, −34.4 kcal/mol (Table 2), is consistent with a reasonable level of stability. Table 4 shows ΔH for the two $AlO + O_2$ reactions to be 24.4 kcal/mol for producing $AlO_2 + O$ and −53.3 kcal/mol for AlO_3.

Another point of interest relates to the strength of the AlO_2 bond formed in the process $AlO + O_2 \rightarrow AlO_2 + O$. Ho and Burns reported this to be 100 ± 9 kcal/mol,[40] on the basis of Al_2O_3 evaporation/mass spectrometry studies, whereas Rogowski et al argued that kinetic data indicate the bond energy to be at least 127 kcal/mol.[41] Although there is some question as to which AlO_2 isomer this is,[41] the largest value that our heats of formation (Table 2) permit is 95.4 kcal/mol, which supports Ho and Burns.

Complexes of Al and AlO with CO and CO_2 have received considerable attention in relation to aluminum combustion.[13,14,41−46] The interaction energies of Al with either one or two CO molecules were predicted by Balaji et al, on the basis of MP2 calculations, to be 4.04 kcal/mol for AlCO and 17.15 kcal/mol for $Al(CO)_2$.[44] These were used by McQuaid and Gole in analyzing the populations of AlO states produced in the O_3 oxidation of AlCO and $Al(CO)_2$.[13] At the CBS-QB3 level, we found these energies to be somewhat larger, 10.0 and 23.9 kcal/mol, respectively (Table 4), but this should not have a major impact upon McQuaid and Gole's conclusions.[13] It is notable that AlO complexes with CO and CO_2 even less strongly than does Al (Table 4).

E. Free Energy Changes and Equilibrium Constants. Table 5 presents ΔG(298 K) and ΔG(2000 K), calculated from the data in Table 1, for the same group of reactions as those in Table 3. Comparison with experimental results shows that the average absolute difference at 298 K is only 1.7 kcal/mol, which is comparable to what was obtained for ΔH(298 K) and ΔH(2000 K) in Table 3. Unlike ΔH, however, ΔG(2000 K) can differ quite considerably from ΔG(298 K), and the computed values are also significantly less accurate. (In Table 5, the average absolute error at 2000 K is 5.9 kcal/mol.) Both of these

TABLE 1: Computed (CBS-QB3) Energy Minima, Enthalpies, and Free Energies at 298 and 2000 K, in Hartree[a]

atom or molecule	$E_{\min}$	H(298 K)	G(298 K)	H(2000 K)	G(2000 K)
H	−0.49982	−0.49746	−0.51047	−0.48398	−0.60142
C	−37.78539	−37.78303	−37.79993	−37.76955	−37.91310
N	−54.52055	−54.51819	−54.53558	−54.50471	−54.65154
O	−74.98764	−74.98528	−75.00259	−74.97180	−75.11808
F	−99.64311	−99.64075	−99.65792	−99.62727	−99.77261
Al	−241.92881	−241.92645	−241.94412	−241.91298	−242.06165
Cl	−459.68364	−459.68128	−459.69932	−459.66781	−459.81894
H_2	−1.17605	−1.16277	−1.17757	−1.14302	−1.28563
N_2	−109.40398	−109.39516	−109.41690	−109.37395	−109.56552
O_2	−150.16841	−150.16140	−150.18467	−150.13920	−150.34318
O_3	−225.19714	−225.18604	−225.21307	-225.15187	−225.40552
F_2	−199.34853	−199.34297	−199.36595	−199.31977	−199.52449
Cl_2	−919.46219	−919.45748	−919.48283	−919.43361	−919.65648
CH	−38.41893	−38.40930	−38.42941	−38.38845	−38.56845
NH	−55.15176	−55.14116	−55.16172	-55.12068	−55.30307
OH	−75.65801	−75.64635	−75.66658	−75.62620	−75.80586
H_2O	−76.35870	−76.33382	−76.35590	−76.30654	−76.51179
HO_2	−150.75406	−150.73627	−150.76225	−150.70567	−150.94401
H_2O_2	−151.40482	−151.37441	−151.40031	−151.33334	−151.59186
HF	−100.36920	−100.35661	-100.37632	−100.33670	−100.51248
AlH	−242.54700	−242.53999	−242.56131	−242.51779	−242.70865
AlH_2	−243.12764	−243.11372	−243.13798	−243.08138	−243.31182
HCl	−460.35468	−460.34477	−460.36595	−460.32403	−460.51106
CN	−92.59244	−92.58428	−92.60727	−92.56275	−92.76332
CO	−113.18726	−113.17895	−113.20138	−113.15750	−113.35417
CO_2	−188.38399	−188.36882	−188.39309	−188.33424	−188.56941
CF_4	−437.12234	−437.10070	−437.13177	−437.03811	−437.37757
NO	−129.75316	−129.74537	−129.76867	−129.72364	−129.92672
NO_2	−204.86106	−204.84844	−204.87633	−204.81529	−205.07208
N_2O	−184.46207	−184.44737	−184.47231	−184.41248	−184.65304
NF	−154.28752	−154.28158	−154.30575	−154.25866	−154.47054
NF_3	−353.78066	−353.76607	−353.79573	−353.71637	−354.02099
AlN	−296.54322	−292.53813	−296.56342	−296.51457	−296.73592
NCl	−514.30683	−514.30166	−514.32709	−514.27816	−514.50029
AlO, **1**	−317.10812	−317.10263	−317.12743	−317.07938	−317.29647
AlO_2, **2**	−392.24896	−392.23988	−392.26793	−392.20110	−392.47379
AlO_2, **3**	−392.20779	−392.19888	−392.22856	−392.16300	−392.44007
AlO_2, **4**	−392.18239	−392.17343	−392.20407	−392.13757	−392.42110
AlO_3, **5**	−467.36254	−467.34891	−467.38167	−467.29838	−467.62701
Al_2O, **6**	−559.12287	−559.11419	−559.14553	−559.07505	−559.37127
Al_2O, **7**	−559.25549	−559.24662	−559.27588	−559.20765	−559.48921
Al_2O, **8**	−559.14785	−559.13963	−559.17069	−559.10324	−559.39115
Al_2O_2, **9**	−634.41681	−634.40336	−634.43682	−634.34961	−634.69076
Al_2O_2, **10**	−634.30516	−634.29189	−634.32543	−634.23798	−634.58029
Al_2O_2, **11**	−634.42888	−634.41599	−634.44675	−634.36495	−634.68140
Al_2O_3, **12**	−709.56873	−709.55060	−709.58667	−709.48214	−709.87206
Al_2O_3, **13**	−709.57145	−709.55423	−709.58999	−709.48824	−709.87014
Al_2O_3,**14**	−709.52528	−709.50824	−709.54559	−709.44205	−709.83559
Al_2O_4, **15**	−784.72843	−784.70706	−784.74550	−784.62597	−785.05821
Al_2O_4, **16**	−784.69294	−784.67115	−784.70956	−784.59038	−785.02141
Al_3O_2, **17**	−876.49991	−876.48383	−876.52512	−876.41685	−876.83966
Al_3O_2, **18**	−876.47844	−876.46304	−876.50178	−876.39556	−876.80275
Al_3O_3, **19**	−951.73939	−951.71831	−951.75922	−951.63697	−952.08673
Al_3O_3, **20**	−951.71796	−951.69772	−951.73661	−951.61573	−952.05405
ClO	−534.77290	−534.76773	−534.79288	−534.74423	−534.96449
ClO_2	−609.86055	−609.85110	−609.88036	−609.81568	−610.08825
AlF	−341.83289	−341.82773	−341.85218	−341.80422	−342.01980
AlF_2	−441.64654	−441.63787	−441.66805	−441.60182	−441.88268
AlF_3	−541.54225	−541.52920	−541.56079	−541.47824	−541.80030
AlCl	−701.80991	−701.80532	−701.83125	−701.78135	−702.00846
$AlCl_2$	−1161.60846	−1161.60101	−1161.63402	−1161.56399	−1161.86717
$AlCl_3$	−1621.48259	−1621.47158	−1621.50727	−1621.41899	−1621.77412
HCO	−113.71776	−113.70116	−113.72663	−113.67037	−113.90520
HNO	−130.33709	−130.31959	−130.34464	−130.28936	−130.51993
HONO	−205.49541	−205.47114	−205.49933	−205.42699	−205.70785
F_2CO	−312.73092	−312.71278	−312.74285	−312.66556	−312.96592
AlOH	−317.80157	−317.78532	−317.81227	−317.75008	−318.00748
HAlO	−317.73536	−317.72260	−317.74778	−317.68641	−317.93235
AlCN	−334.70755	−334.69594	−334.72474	−334.65869	−334.93292
AlNC	−334.71727	−334.70587	−334.73497	−334.66854	−334.94482
AlCO[b]	−355.13217	−355.12128	−355.15076	−355.08361	−355.36341
AlOC[b]	−355.11777	−355.10666	−355.14116	−355.06902	−355.38286
AlCO[c]	−355.11657	−355.10686	−355.13788	−355.07145	−355.35663
$Al(CO)_2$	−468.34333	−468.32245	−468.35906	−468.25865	−468.64158
$AlCO_2$	−430.33836	−430.32264	−430.35563	−430.27353	−430.59982
OAlCO	−430.30070	−430.28596	−430.32409	−430.23591	−430.60042
$OAlCO_2$	−505.48911	−505.46883	−505.50511	−505.40492	−505.78469
FAlO	−416.98151	−416.97176	−416.99978	−416.93348	−417.20441
ClAlO	−776.96525	−776.95608	−776.98545	−776.91734	−777.19892

TABLE 1: (Continued)

atom or molecule	E_{min}	H(298 K)	G(298 K)	H(2000 K)	G(2000 K)
FAlCl	−801.62707	−801.61901	−801.65127	−801.58247	−801.87898
$HAlCl_2$	−1162.24835	−1162.23331	−1162.26615	−1162.18362	−1162.51090
HAl(O)F	−417.55386	−417.53777	−417.56933	−417.48892	−417.80469
HOAlF	−417.61838	−417.59827	−417.62996	−417.55089	−417.86527
HAl(O)Cl	−777.53434	−777.51893	−777.55193	−777.46954	−777.79680
HOAlCl	−777.59936	−777.57988	−777.61304	−777.53199	−777.85801

[a] One hartree = 627.509 kcal/mol. [b] Linear. [c] Cyclic.

TABLE 2: Calculated and Experimental Gas Phase Heats of Formation at 298 K, in kcal/mol

atom or molecule	calcd	exptl[a]	atom or molecule	calcd	exptl[a]
H	52.7	52.10311	Al_2O_3, **12**	−128.3	
C		171.288	Al_2O_3, **13**	−130.6	
N	112.6	112.974	Al_2O_3, **14**	−101.7	
O	59.9	59.5538	Al_2O_4, **15**	−175.8	
F	19.3	18.9747	Al_2O_4, **16**	−153.3	
Al		78.8	Al_3O_2, **17**	−104.4	
Cl	29.8	28.9919	Al_3O_2, **18**	−91.3	
O_3	35.2	34.1	Al_3O_3, **19**	−200.9	
CH	143.1	142	Al_3O_3, **20**	−188.0	
NH	86.5	90	ClO	26.2	24.1919
OH	9.9	9.318131	ClO_2	24.5	25
H_2O	−56.7	−57.7979	AlF	−65.4	−63.5
HO_2	4.1	0.5	AlF_2	−152.4	*d*
H_2O_2	−31.5	−32.53021	AlF_3	−290.4	−289.0349
HF	−65.1	−65.14011	AlCl	−15.4	−12.3
AlH	58.6	62	$AlCl_2$	−57.4	*d*
AlH_2	63.4		$AlCl_3$	−146.4	−139.72
HCl	−21.7	−22.0631	HCO	10.6	10.4
CN	106.2	104	HNO	25.1	23.8
CO	−26.5	−26.41661	HONO	−19.3	−18.3401
CO_2	−95.0	−94.05411	F_2CO	−146.3	−149.1[e]
CF_4	−225.1	−223.04	AlOH	−44.7	−43
NO	20.7	21.5801	HAlO	−5.3	*d*
NO_2	6.6	7.9099	AlCN	68.8	71.92[f]
N_2O	17.9	19.61	AlNC	62.6	66.49[f]
NF	54.9	*d*	AlCO[b]	42.3	
NF_3	−33.9	−31.57	AlOC[b]	51.5	
AlN	132.7	*d*	AlCO[c]	51.4	
NCl	78.2		$Al(CO)_2$	1.9	
AlO, **1**	18.9	16	$AlCO_2$	−33.4	
AlO_2, **2**	−16.6	*d*	OAlCO	−10.4	
AlO_2, **3**	9.1		$OAlCO_2$	−74.5	
AlO_2, **4**	25.1		FAlO	−105.1	*d*
AlO_3, **5**	−34.4		ClAlO	−59.4	*d*
Al_2O, **6**	44.3		FAlCl	−104.6	*d*
Al_2O, **7**	−38.8	*d*	$HAlCl_2$	−89.4	
Al_2O, **8**	28.3		HAl(O)F	−95.5	
Al_2O_2, **9**	−86.5		HOAlF	−133.5	
Al_2O_2, **10**	−16.6		HAl(O)Cl	−47.7	
Al_2O_2, **11**	−94.5	*d*	HOAlCl	−86.0	

[a] Unless otherwise indicated, experimental data are from ref 1. [b] Linear. [c] Cyclic. [d] Value given in ref 1 appears to have substantial uncertainty; see text. [e] Asher, R. L.; Appelman, E. H.; Ruscic, B. *J. Chem. Phys.* **1996**, *105*, 9781. [f] Meloni, G.; Gingerich, K. A. *J. Chem. Phys.* **1999**, *111*, 969.

TABLE 3: Comparison of Calculated and Experimental Heats of Reaction, in kcal/mol

reaction	ΔH(298 K)		ΔH(2000 K)	
	calc	exp[a]	calc	exp[a]
$AlO + HF \rightarrow AlF + OH$	−9.3	−5	−9.0	−6
$O + H_2O \rightarrow 2OH$	16.6	16.9	16.3	16.7
$AlH + HF \rightarrow AlF + H_2$	−58.9	−60	−58.2	−59
$AlO + H_2 \rightarrow AlOH + H$	−10.9	−7	−7.3	−7
$H + O_2 \rightarrow OH + O$	17.1	16.8	15.8	15.6
$AlH + F_2 \rightarrow AlF + HF$	−189.1	−191	−190.4	−192
$AlOH + F \rightarrow AlO + HF$	−20.8	−25	−24.3	−25
$CO + OH \rightarrow CO_2 + H$	−25.7	−24.9	−21.7	−21.0
$AlH + O_2 \rightarrow AlOH + O$	−43.4	−45	−40.7	−45
$CO + H_2 \rightarrow HCO + H$	89.8	88.9	91.7	90.7
$Cl + HCO \rightarrow HCl + CO$	−88.7	−87.9	−90.0	−89.6
$AlF + H_2O \rightarrow AlOH + HF$	12.3	13	15.0	13
$CO + O_2 \rightarrow CO_2 + O$	−8.6	−8.1	−5.9	−5.4
$F + H_2O \rightarrow HF + OH$	−17.8	−17.0	−18.3	−17.6
$F + HCO \rightarrow HF + CO$	−121.5	−120.9	−123.3	−122.9

[a] Reference 1.

features, which have been noted previously,[18,20,21] reflect the formula $\Delta G = \Delta H - T\Delta S$, with ΔS being the change in entropy. Although temperature variations in ΔS are small,[20] the nearly 7-fold increase in T between 300 and 2000 K greatly magnifies its contribution to ΔG, as well as that of any error in its calculation.

Equilibrium constants can be determined by means of the relationship[47] $K_{eq} = \exp(-\Delta G°/RT)$, taking the free energies in Table 1 to be standard state values. In Table 6 are the computed equilibrium constants relating the various isomers in Table 1, evaluated at both 298 and 2000 K. At 298 K, in most instances, one isomer greatly predominates, sometimes overwhelmingly so. However, the situation is markedly different at 2000 K. The proportions of the isomers become much less disparate, so that more of them can be expected to be present in significant amounts. This is true even when ΔG is approximately the same at the two temperatures and is a consequence of the form of the expression for K_{eq}; increasing the temperature causes K_{eq} to move toward unity.

The same is of course true for any of the reactions in Table 4. For example, equilibrium constants obtained from the free energies in Table 1 show that the process $Al_2O + O_2 \rightarrow AlO + AlO_2$ essentially does not occur at 298 K ($K_{eq} \sim 10^{-30}$) but becomes appreciable at 2000 K ($K_{eq} \sim 10^{-4}$). On the other hand, $Al + H_2O \rightarrow AlOH + H$ occurs to a much lesser extent at 2000 K ($K_{eq} \sim 10^{2}$) than at 298 K ($K_{eq} \sim 10^{10}$). Thus, the importance of the various ignition and combustion steps and the corresponding products is very dependent upon the temperature.

It is important to note that the uncertainty in the calculated ΔG(2000 K), pointed out above, does not translate into a corresponding one for K_{eq}(2000 K). Whereas, at 298 K, an error in ΔG of only ± 1.4 kcal/mol suffices to change K_{eq} by an order of magnitude, at 2000 K, the same consequence requires an error of more than 9 kcal/mol.

F. Reaction Mechanisms. We have investigated the mechanisms of the reactions

$$Al + O_2 \rightarrow AlO + O \tag{1}$$

$$Al + CO_2 \rightarrow AlO + CO \tag{2}$$

$$AlO + HCl \rightarrow ClAlO + H \tag{3}$$

$$AlO + HCl \rightarrow AlOH + Cl \tag{4}$$

$$AlCl + O_2 \rightarrow ClAlO + O \tag{5}$$

Their activation barriers and transition states, plus one intermediate, are reported in Table 7 and Figure 3. Also included in Table 7 are the results for four other reactions that were studied in our analyses of boron ignition/combustion[19,21] but are equally

TABLE 4: Calculated and Experimentala Gas Phase Heats of Reaction at 298 K, in kcal/mol^b

reaction	Δ*H*(298 K), calc^b	Δ*H*(298 K), exp^a	reaction	Δ*H*(298 K), calc^b	Δ*H*(298 K), exp^a
$Al + O \rightarrow AlO$	−119.8	−122	$AlO + F_2 \rightarrow FAlO + F$	−104.7	
$Al + O_2 \rightarrow AlO + O$	0.0	−3	$AlO + Cl_2 \rightarrow ClAlO + Cl$	−48.5	
$Al + O_3 \rightarrow AlO + O_2$	−95.1	−97	$AlO + Cl_2 \rightarrow AlCl + ClO$	−8.1	−4
$Al + N \rightarrow AlN$	−58.7		$AlO_2 + O \rightarrow AlO_3$	−77.7	
$Al + N_2 \rightarrow AlN + N$	166.5		$2AlO_2 \rightarrow Al_2O_3 + O$	−37.5	
$Al + OH \rightarrow AlOH$	−133.4	−131	$Al_2O + O \rightarrow 2AlO$	16.7	
$Al + OH \rightarrow AlO + H$	−17.1	−20	$Al_2O + O \rightarrow Al_2O_2$	−115.5	
$Al + H_2O \rightarrow AlO + H_2$	−3.2	−5	$Al_2O + O_2 \rightarrow 2AlO + O$	136.5	
$Al + H_2O \rightarrow AlOH + H$	−14.1	−12	$Al_2O + O_2 \rightarrow Al_2O_2 + O$	4.2	
$Al + H_2O \rightarrow AlH + OH$	46.4	50	$Al_2O + O_2 \rightarrow AlO + AlO_2$	41.1	
$Al + AlO \rightarrow Al_2O$	−136.5		$Al_2O + O_2 \rightarrow Al_2O_3$	−91.7	
$Al + AlO_2 \rightarrow 2AlO$	−24.4	−26	$Al_2O_2 + O \rightarrow Al_2O_3$	−96.0	
$Al + AlO_2 \rightarrow Al_2O_2$	−156.7		$AlH + O_2 \rightarrow AlOH + O$	−43.4	−45
$Al + Al_2O_2 \rightarrow AlO + Al_2O$	−4.3		$AlO + CO_2 \rightarrow AlO_2 + CO$	33.0	31
$Al + CO \rightarrow AlCO$	−10.0		$AlO + CO_2 \rightarrow OAlCO_2$	1.6	
$Al + 2CO \rightarrow Al(CO)_2$	−23.9		$AlO + N_2O \rightarrow AlO_2 + N_2$	−53.4	−56
$Al + CO_2 \rightarrow AlCO_2$	−17.2		$AlO + HF \rightarrow HAl(O)F$	−49.3	
$Al + CO_2 \rightarrow AlO + CO$	8.6	5	$AlO + HCl \rightarrow HAl(O)Cl$	−44.9	
$Al + N_2O \rightarrow AlO + N_2$	−77.8	−82	$AlO + HF \rightarrow HOAlF$	−87.2	
$Al + N_2O \rightarrow AlN + NO$	56.7		$AlO + HCl \rightarrow HOAlCl$	−83.1	
$AlO + O_2 \rightarrow AlO_2 + O$	24.4	23	$AlO + HF \rightarrow FAlO + H$	−6.3	
$AlO + O_2 \rightarrow AlO_3$	−53.3		$AlO + HCl \rightarrow ClAlO + H$	−3.9	
$2AlO \rightarrow Al_2O + O$	−16.7		$AlO + HF \rightarrow AlF + OH$	−9.3	−5
$2AlO \rightarrow Al_2O_2$	−132.2		$AlO + HCl \rightarrow AlCl + OH$	−2.7	3
$AlO + AlO_2 \rightarrow Al_2O_3$	−132.9		$AlO + HF \rightarrow AlOH + F$	20.8	25
$AlO + Al_2O_2 \rightarrow Al_2O + AlO_2$	20.2		$AlO + HCl \rightarrow AlOH + Cl$	−12.0	−8
$AlO + CO \rightarrow OAlCO$	−2.7		$AlO + F_2 \rightarrow FAlO + F$	−104.7	
$AlO + CO_2 \rightarrow AlO_2 + CO$	33.0	31	$AlO + Cl_2 \rightarrow ClAlO + Cl$	−48.5	
$AlO + CO_2 \rightarrow OAlCO_2$	1.6		$AlO + Cl_2 \rightarrow AlCl + ClO$	−8.1	−4
$AlO + N_2O \rightarrow AlO_2 + N_2$	−53.4	−56	$AlO_2 + O \rightarrow AlO_3$	−77.7	
$AlO + HF \rightarrow HAl(O)F$	−49.3		$2AlO_2 \rightarrow Al_2O_3 + O$	−37.5	
$AlO + HCl \rightarrow HAl(O)Cl$	−44.9		$Al_2O + O \rightarrow 2AlO$	16.7	
$AlO + HF \rightarrow HOAlF$	−87.2		$Al_2O + O \rightarrow Al_2O_2$	−115.5	
$AlO + HCl \rightarrow HOAlCl$	−83.1		$Al_2O + O_2 \rightarrow 2AlO + O$	136.5	
$AlO + HF \rightarrow FAlO + H$	−6.3		$Al_2O + O_2 \rightarrow Al_2O_2 + O$	4.2	
$AlO + HCl \rightarrow ClAlO + H$	−3.9		$Al_2O + O_2 \rightarrow AlO + AlO_2$	41.1	
$AlO + HF \rightarrow AlF + OH$	−9.3	−5	$Al_2O + O_2 \rightarrow Al_2O_3$	−91.7	
$AlO + HCl \rightarrow AlCl + OH$	−2.7	3	$Al_2O_2 + O \rightarrow Al_2O_3$	−96.0	
$AlO + HF \rightarrow AlOH + F$	20.8	25	$AlH + O_2 \rightarrow AlOH + O$	−43.4	−45
$AlO + HCl \rightarrow AlOH + Cl$	−12.0	−8			

[a] Reference 1. [b] When Table 1 includes two or more isomeric forms of a particular reactant or product, then unless otherwise indicated, the most stable has been used in finding Δ*H*(298 K).

TABLE 5: Comparison of Calculated and Experimental Free Energy Changes, in kcal/mol

	Δ*G*(298 K)		Δ*G*(2000 K)	
reaction	calc	exp^a	calc	exp^a
$AlO + HF \rightarrow AlF + OH$	−9.4	−6.	−10.5	−9.
$O + H_2O \rightarrow 2OH$	15.9	15.6	11.4	7.7
$AlH + HF \rightarrow AlF + H_2$	−57.8	−59.	−52.9	−54.
$AlO + H_2 \rightarrow AlOH + H$	−11.1	−6.	−16.8	2.
$H + O_2 \rightarrow OH + O$	16.3	15.0	13.0	5.7
$AlH + F_2 \rightarrow AlF + HF$	−189.0	−191.	−187.7	−188.
$AlOH + F \rightarrow AlO + HF$	−21.1	−26.	−18.1	−33.
$CO + OH \rightarrow CO_2 + H$	−22.3	−21.1	−6.8	−3.0
$AlH + O_2 \rightarrow AlOH + O$	−43.2	−44.	−46.3	−37.
$CO + H_2 \rightarrow HCO + H$	89.0	88.1	83.6	82.7
$Cl + HCO \rightarrow HCl + CO$	−88.7	−87.5	−88.5	−83.9
$AlF + H_2O \rightarrow AlOH + HF$	12.2	14.	7.3	20.
$CO + O_2 \rightarrow CO_2 + O$	−6.0	−6.1	6.2	2.7
$F + H_2O \rightarrow HF + OH$	−18.2	−17.7	−21.3	−21.9
$F + HCO \rightarrow HF + CO$	−121.2	−120.1	−118.5	−113.7

[a] Reference 1.

TABLE 6: Computed Properties of Isomeric Equilibria

equilibrium	Δ*G* (298 K)^a	K_{eq} (298 K)	Δ*G* (2000 K)^a	K_{eq} (2000 K)
AlO_2, **2** ↔ AlO2, **3**	24.7	7.8×10^{-19}	21.2	4.9×10^{-3}
AlO_2, **2** ↔ AlO2, **4**	40.1	4.2×10^{-30}	33.1	2.4×10^{-4}
AlO_2, **3** ↔ AlO_2, **4**	15.4	5.4×10^{-12}	11.9	5.0×10^{-2}
Al_2O, **6** ↔ Al_2O, **7**	−81.8	9.0×10^{59}	−74.0	1.2×10^{8}
Al_2O, **6** ↔ Al_2O, **8**	−15.8	3.7×10^{11}	−12.5	2.3×10^{1}
Al_2O, **7** ↔ Al_2O, **8**	66.0	4.1×10^{-49}	61.5	1.9×10^{-7}
Al_2O_2, **9** ↔ Al_2O_2, **10**	69.9	5.8×10^{-52}	69.3	2.7×10^{-8}
Al_2O_2, **9** ↔ Al_2O_2, **11**	−6.2	3.7×10^{4}	5.9	2.3×10^{-1}
Al_2O_2, **10** ↔ Al_2O_2, **11**	−76.1	6.4×10^{55}	−63.4	8.6×10^{6}
Al_2O_3, **12** ↔ Al_2O_3, **13**	−2.1	3.4×10^{1}	1.2	7.4×10^{-1}
Al_2O_3, **12** ↔ Al_2O_3, **14**	25.8	1.3×10^{-19}	22.9	3.2×10^{-3}
Al_2O_3, **13** ↔ Al_2O_3, **14**	27.9	3.8×10^{-21}	21.7	4.3×10^{-3}
Al_2O_4, **15** ↔ Al_2O_4, **16**	22.6	2.9×10^{-17}	23.1	3.0×10^{-3}
Al_3O_2, **17** ↔ Al_3O_2, **18**	14.6	1.8×10^{-11}	23.2	2.9×10^{-3}
Al_3O_3, **19** ↔ Al_3O_3, **20**	14.2	4.0×10^{-11}	20.5	5.7×10^{-3}
AlOH ↔ HAlO	40.5	2.2×10^{-30}	47.1	7.1×10^{-6}
AlCN ↔ AlNC	−6.4	5.1×10^{4}	−7.5	6.5
AlCO^b ↔ AlOC^b	6.0	3.8×10^{-5}	−12.2	2.2×10^{1}
AlCO^b ↔ AlCOc	8.1	1.2×10^{-6}	4.3	3.4×10^{-1}
AlOC^b ↔ AlCO^c	2.1	3.1×10^{-2}	16.5	1.6×10^{-2}
$AlCO_2$ ↔ OAlCO	19.8	3.1×10^{-15}	−0.4	1.1
HAl(O)F ↔ HOAlF	−38.0	7.7×10^{27}	−38.0	1.4×10^{4}
HAl(O)Cl ↔ HOAlCl	−38.3	1.3×10^{28}	−38.4	1.6×10^{4}

[a] Units are kcal/mole. [b] Linear. [c] Cyclic.

relevant for aluminum. In related work, Swihart and Catoire have recently used several different correlated methods to determine the transition states and activation barriers of a group of Al, H, and Cl reactions.[48]

Reaction 1, $Al + O_2 \rightarrow AlO + O$, has some interesting features. The dissociation energies of O_2 and AlO are very similar, as can be verified with the data in Table 2; accordingly, Δ*H* for this reaction is close to zero at both 298 and 2000 K. The equilibrium constants at the two temperatures are 3.7 and 4.6, respectively (using free energies from Table 1). Furthermore, we were unable to find a doublet transition state (although we did locate a quartet, with an activation energy of 24.7 kcal/mol). This is fully consistent with Garland and Nelson's conclusion, based upon the measured temperature dependence

TABLE 7: Calculated Activation Enthalpies and Overall Heats of Reaction at 298 K, in kcal/mol (TS = transition state)[a]

reaction	ΔH_{act}	$\Delta H_{overall}$ calc	$\Delta H_{overall}$ exp[b]
(1) $Al + O_2 \rightarrow AlO + O$	0.0	0.0	−3
(2) $Al + CO_2 \rightarrow TS2 \rightarrow AlO + CO$	14.4	8.6	5
(3) $AlO + HCl \rightarrow TS3 \rightarrow ClAlO + H$	12.3	−3.9	
(4) $AlO + HCl \rightarrow AlOH + Cl$		−12.0	−8
(a) $AlO + HCl \rightarrow AlOHCl$	0.0	−12.6	
(b) $AlOHCl \rightarrow AlOH + Cl$	0.0	0.5	
(5) $AlCl + O_2 \rightarrow TS5 \rightarrow ClAlO + O$	28.3	15.9	
(6) $O + H_2 \rightarrow TS6 \rightarrow H + OH$	10.2	2.7	1.9
(7) $F + H_2O \rightarrow TS7 \rightarrow HF + OH$	13.4	−17.8	−17.0
(8) $O + H_2O \rightarrow TS8 \rightarrow 2OH$	17.7	16.6	16.9
(9) $CO + OH \rightarrow CO_2 + H$		−25.7	−24.9
(a) $CO + OH \rightarrow$ *trans*-OCOH	0.0	−27.1	
(b) *trans*-OCOH $\rightarrow$ TS9A $\rightarrow$ *cis*-OCOH	8.1	2.0	
(c) *cis*-OCOH $\rightarrow$ TS9B $\rightarrow$ $CO_2 + H$	24.3	−0.6	

[a] The results for reactions 6−9 are taken from refs 19 and 21; the latter includes the structures of the corresponding transition states and intermediates. [b] Reference 1.

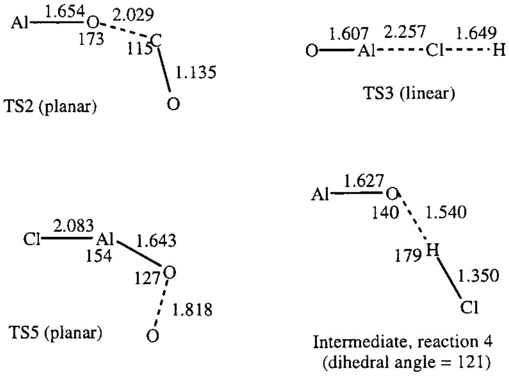

Figure 3. Computed bond lengths (Å) and angles (deg) in transition states and intermediate in reactions 1−5. (Those for the other reactions can be found in reference 21).

of the rate constant, that this reaction has a near-zero barrier.[49] Evidently, one oxygen can move essentially freely between the aluminum and the other oxygen, with no significant preference for either.

A further aspect of this reaction is the possibility of forming AlOO (**4**), the least stable isomer of AlO_2, but which has been observed in matrix studies.[50] The computed enthalpies and free energies in Table 1 show that AlOO is about 54 kcal/mol lower in enthalpy than either the reactants $Al + O_2$ or the products $AlO + O$, at both 298 and 2000 K, and at 298 K it is about 47 kcal/mol lower in free energy. At the lower temperature, therefore, the formation of AlOO is clearly an attractive option. At 2000 K, however, the computed free energy barrier for AlOO returning to $Al + O_2$ diminishes to 10.2 kcal/mol, and it is only 4.1 kcal/mol for going on to $AlO + O$. The respective equilibrium constants are 7.7×10^{-2} and 3.6×10^{-1}. It was pointed out above that the calculated ΔG(2000 K) values have a sizable uncertainty but that this is less so for the corresponding equilibrium constants. Thus, it seems safe to say that at 2000 K (unlike 298 K), there is a significant probability of AlOO proceeding to $AlO + O$ (or somewhat less likely, going back to $Al + O_2$).

The importance of reaction 2 lies in the belief that CO_2 oxidation of aluminum is a major route to Al_2O_3.[7,51] The considerable interest in the various complexes of Al and AlO with CO and CO_2 has been mentioned earlier.[13,14,41−46]

Experimental studies of reactions 3−5 have been carried out by Fontijn and co-workers.[14,52] They pointed out[14] that there may be an intermediate complex involved in reactions 3 and/or 4, which we did find to be the case for the latter. Even though the second step in reaction 4 is slightly endothermic, its calculated equilibrium constant at 298 K is 3.8×10^3.

Finally, reaction 9 involves two intermediates and three steps, the last two of which go through transition states.[21] A similar description has been presented by Bradley and Schatz.[53]

IV. Summary

We have carried out extensive CBS-QB3 calculations relating to the thermodynamics of aluminum ignition and combustion in oxygen/nitrogen/fluorine environments. The data presented in this paper permit the determination of the heats of reaction and equilibrium constants, at 298 and 2000 K, of numerous possible intermediate steps in these processes. The average absolute differences from experiment of ΔH(298 K), ΔH(2000 K), and ΔG(298 K) are all less than 2.0 kcal/mol. Although the ΔG(2000 K) are significantly less accurate, this fortunately does not translate into commensurate errors in the equilibrium constants at 2000 K. For a few reactions, we have also investigated the mechanisms, identifying intermediates and transition states and computing the activation barriers.

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References and Notes

(1) Mallard, W. G., Linstrom, P. J., Eds.; *NIST Chemistry Webbook*, NIST Standard Reference Database No. 69; National Institute of Standards and Technology: Gaithersburg, MD, 1998 (http://webbook.nist.gov).

(2) Price, E. W.; Kraeutle, K. J.; Prentice, J. L.; Boggs, T. L.; Crump, J. E.; Zurn, D. E. *Behavior of Aluminum in Solid Propellant Combustion*, NWC TP 6120; Naval Air Warfare Center: China Lake, CA, 1982.

(3) Price, E. W. *Prog. Astronaut. Aeronaut.* **1984**, *6*, 479.

(4) Oblath, S. B.; Gole, J. L. *Combust. Flame* **1980**, *37*, 293.

(5) Driscoll, J. F.; Nicholls, J. A.; Patel, V.; Shahidi, B. K.; Liu, T. C. *AIAA J.* **1986**, *24*, 856.

(6) Parr, T. P.; Hanson-Parr, D. M. *Proc. 23rd JANNAF Combust. Comm. Mtg.*, Vol. I, CPIA Pub. **1986**, *457*, 249.

(7) Yuasa, S.; Sogo, S.; Isoda, H. *Twenty-Fourth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1992; p 1817.

(8) Brooks, K. P.; Beckstead, M. W. *J. Propul. Power* **1995**, *11*, 769.

(9) Belyung, D. P.; Fontijn, A. *J. Phys. Chem.* **1995**, *99*, 12225.

(10) Dreizin, E. L. *Combust. Flame* **1996**, *105*, 541.

(11) Bucher, P.; Yetter, R. A.; Dryer, F. L.; Parr, T. P.; Hanson-Parr, D. M.; Vicenzi, E. P. *Twenty-Sixth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1996; p 1899.

(12) Widener, J. F.; Beckstead, M. W. *AIAA 98-3824*; 34th AIAA/ASME/SAE/ASEE Joint Propulsion Conference: Cleveland, OH, 1998.

(13) McQuaid, M. J.; Gole, J. L. *Chem. Phys.* **1998**, *234*, 297.

(14) Belyung, D. P.; Dalakos, G. T.; Rocha, J.-D. R.; Fontijn, A. *Twenty-Seventh Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1998; Vol. 1, p 227.

(15) Bucher, P.; Yetter, R. T.; Dryer, F. L.; Parr, T. P.; Hanson-Parr, D. M. *Twenty- Seventh Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1998; Vol. 2, p 2421.

(16) Fontijn, A. *Combust. Sci. Technol.* **1986**, *50*, 151.

(17) Swihart, M. T.; Catoire, L. *Combust. Flame* **2000**, *121*, 210.

(18) Politzer, P.; Lane, P.; Concha, M. C. *J. Phys. Chem. A* **1999**, *103*, 1419.

(19) Politzer, P.; Lane, P.; Concha, M. C. *Proc. 36th JANNAF Combust. Subcomm. Mtg.*, Vol. II, **2000**, *691*, 331.

(20) Politzer, P.; Concha, M. C.; Lane, P. *J. Mol. Struct. (THEOCHEM)* **2000**, *529*, 41.

(21) Politzer, P.; Lane, P.; Concha, M. *Rec. Res. Dev. Phys. Chem.* In press.

(22) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.;

Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(24) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986.

(25) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154.

(26) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(27) Lide, D. R., Ed.; *Handbook of Chemistry and Physics*, 78th ed.; CRC Press: Boca Raton, FL, 1997.

(28) Utkin, A. N.; Girichev, G. V.; Giricheva, N. I.; Khaustov, S. V. *J. Struct. Chem.* **1986**, *27*, 212.

(29) Aarset, K.; Shen, Q.; Thomassen, H.; Richardson, A. D.; Hedberg, K. *J. Phys. Chem. A* **1999**, *103*, 1644.

(30) Nemukhin, A. V.; Weinhold, F. *J. Chem. Phys.* **1992**, *97*, 3420.

(31) Desai, S. R.; Wu, H.; Rohlfing, C. M.; Wang, L.-S. *J. Chem. Phys.* **1997**, *106*, 1309.

(32) Ghanty, T. K.; Davidson, E. R. *J. Phys. Chem. A* **1999**, *103*, 8985.

(33) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(34) Chen, W.; Hase, W. L.; Schlegel, H. B. In *Gas-Phase Metal Reactions*, Fontijn, A., Ed., Elsevier: Amsterdam, 1992, ch. 9.

(35) Xantheas, S. S.; Dunning, T. H., Jr.; Mavridis, A. *J. Chem. Phys.* **1997**, *106*, 3280.

(36) Petrie, S. *J. Phys. Chem. A* **1998**, *102*, 7828.

(37) Boo, B. H.; Liu, Z. *J. Phys. Chem. A* **1999**, *103*, 1250.

(38) Bauschlicher, Jr., C. W.; Ricca, A. *J. Phys. Chem. A* **1999**, *103*, 4313.

(39) Andrews, L.; Borkholder, T. R.; Yustein, J. T. *J. Phys. Chem.* **1992**, *96*, 6, 10182.

(40) Ho, P.; Burns, R. P. *High Temp. Sci.* **1980**, *12*, 31.

(41) Rogowski, D. F.; English, A. J.; Fontijn, A. *J. Phys. Chem.* **1986**, *90*, 1688.

(42) Kasai, P. H.; Jones, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8018.

(43) Chenier, J. H. B.; Hampson, C. A.; Howard, J. A.; Mile, B.; Sutcliffe, R. *J. Phys. Chem.* **1986**, *90*, 1524.

(44) Balaji, V.; Sumil, K. K.; Jordan, K. D. *Chem. Phys. Lett.* **1987**, *136*, 309.

(45) McQuaid, M.; Woodward, J. R.; Gole, J. L. *J. Phys. Chem.* **1988**, *92*, 252.

(46) Parnis, J. M.; Mitchell, S. A.; Kanigan, T. S.; Hackett, P. A. *J. Phys. Chem.* **1989**, *93*, 8045.

(47) Glasstone, S. *Thermodynamics for Chemists*: Van Nostrand: Princeton, NJ, 1947.

(48) Swihart, M. T.; Catoire, L. *J. Phys. Chem. A* **2001**, *105*, 264.

(49) Garland, N. L.; Nelson, H. H. *Chem. Phys. Lett.* **1992**, *191*, 269.

(50) Sonchik, S. M.; Andrews, L.; Carlson, K. D. *J. Phys. Chem.* **1983**, *87*, 2004.

(51) Widener, J. F.; Beckstead, M. W. *Proc. 34th AIAA/ASME/SAE/ASEE Joint Propuls. Conf.*, paper AIAA 98−3824, 1998.

(52) Slavejkov, A. G.; Stanton, C. T.; Fontijn, A. *J. Phys. Chem.* **1990**, *94*, 3347.

(53) Bradley, K. S.; Schatz, G. C. *J. Chem. Phys.* **1997**, *106*, 8464.