GAS-PHASE METAL REACTIONS
A. Fontijn (editor)

Ab Initio MO Calculations of the Thermochemistry of BX, AlX, OBX and OAlX (X = O, F, Cl)

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Abstract

Bond dissociation energies and heats of formation have been computed for BX, AlX, OBX and OAlX (X = O, F, Cl) at the PMP4/6-31G(d,p), QCISD(T)/6-311G(d,p), G1 and G2 levels of theory. Except for OBCl, OAlF and OAlCl, the G1 and G2 theories give results that are very good agreement with the experimental heats of formation (average absolute deviation of 2.8 kcal/mol). For OBCl, OAlF and OAlCl, the discrepancies are well outside the ±2 kcal/mol average absolute error range found when comparing G1 and G2 calculations with well established experimental values; this suggests that the experimental heats of formation for OBCl, OAlF and OAlCl are in error and need to be re-examined. The G1 and G2 calculations predict $\Delta H^\circ_{f\,0}$ = -94 kcal/mol for OBCl, i.e. 18 kcal/mol more stable than experiment; $\Delta H^\circ_{f\,0}$ for OAlF and OAlCl are calculated to be -103 and -58 kcal/mol, respectively, i.e. 35 and 25 kcal/mol less stable than previously thought.

1. INTRODUCTION

There is a need to understand the fundamental processes of high energy density fuels containing boron and aluminum at a microstructural level. A critical first step to this understanding is the determination of the basic thermodynamics and homogeneous kinetics of various boron and aluminum species in highly combustible environments. A number of experimental papers on the kinetics of boron and aluminum oxidation reactions can be found in this volume [1,2]. The genesis of the present study is a series of papers by Fontijn and others on the oxidation of boron and aluminum monohalides [2-4]. Rate constants have been measured for BF, BCl and AlCl reacting with a number of different oxygen donating species over a wide temperature range. The activation energies extracted from these rate data have been correlated successfully with the bond energies and ionization potentials of the boron and aluminum halides and the electron affinities of the oxidants. P. Marshall, J. D. Goddard and co-workers [5] have studied the reactions of B and Al with O_2 and CO_2 using high level ab initio molecular orbital theory for the structures and energetics and quantum RRK theory for the kinetics. The work we describe in the present paper stems from an on-going study [6] of the mechanism and kinetics of BX and AlX (X = F, Cl) reacting with O_2. In the course of this study we became acutely aware of possible errors in the experimental heats of formation of some of the key intermediates and products of these reactions. In the present paper we have used ab initio molecular orbital calculations at the G1 and G2 levels of theory [7,8] in an effort to estimate a consistent set of bond dissociation energies and heats of formation of the reactants, intermediates and products of the reactions of BX and AlX with O_2.

Relative energies and heats of reaction can be computed reliably at an affordable level of theory if the calculational errors in the reactants and products nearly cancel, such as in isodesmic and isogyric reactions [9]. However, accurate bond dissociation energies and heats of formation are exceedingly difficult to calculate directly because of unbalanced errors due to basis set deficiencies and inadequacies in the treatment of electron correlation energy. To overcome these difficulties, Pople et al. [7,8] have developed the G1 and G2 levels of theory which can reliably calculate energetics to within ±2 kcal/mol of the experimental values. These calculational methods take into account, in an additive fashion, the effects of diffuse s,p functions, multiple sets of polarization functions, higher angular momentum functions, fourth order perturbation theory and quadratic configuration interaction for electron correlation, and an empirical correction for higher order effects. The average absolute deviation for 125 well established energies (atomization energies, ionization energies and electron affinities) is 1.5 kcal/mol for G1 theory and 1.2 kcal/mol for G2 theory [8]. With only 2 exceptions, atomization energies differ from experiment by less than 2 kcal/mol for first row systems and by less than 3 kcal/mol for second row systems. Thus, the G1 and G2 levels of theory should provide suitably reliable estimates of the energetics of species in the present study.

2. METHOD

All electronic structure calculations were carried out using the GAUSSIAN 90 [10] series of programs. Restricted Hartree-Fock was used for closed shell species and unrestricted for open shell. Equilibrium geometries were optimized with the 6-31G(d,p) basis set [11] at the Hartree-Fock level (HF/6-31G(d,p) and at the second order Møller-Plesset perturbation theory level (MP2/6-31G(d,p)). Vibrational frequencies and zero point energies were calculated at the HF/6-31G(d,p) level using the HF optimized geometries. Total energies were calculated by fourth order Møller-Plesset perturbation theory with an approximate spin projection method [12] to correct for spin contamination in the open shell systems (PMP4/6-31G(d,p), frozen core). Total energies were also calculated with a slightly larger basis set using the quadratic configuration interaction method [13] with correction for triple excitations (QCISD(T)/6-311G(d,p), frozen core). More accurate estimates of the total energies were obtained using the G1 and G2 levels of theory.

G1 theory [7] is a procedure for computing total energies from a composite of molecular orbital calculations. Geometries are optimized at the HF/6-31G(d) and MP2/6-31G(d) levels. Zero point energies are calculated at the HF/6-31G(d) level and scaled by 0.8929. Electron correlation energy is computed at the MP4SDTQ/6-311G(d,p) using the MP2/6-31G(d) geometry. To correct for the effect of diffuse functions, the energy is also calculated MP4SDTQ/6-311+G(d,p) level:

$$\Delta E(+) = E(\mathrm{MP4SDTQ/6\text{-}311{+}G(d,p)}) - E(\mathrm{MP4SDTQ/6\text{-}311G(d,p)}) \qquad (1)$$

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Table 1.
Total Energies for AX and OAX (A = B, Al; X = O, F, Cl)[a,b]

Species	State	6-31G(d,p)	6-311G(d,p)	6-311G(2df,p)	6-311+G(3df,2p)
		PMP4	QCISD(T)	MP4	MP2
B		-24.57623	-24.59177	-24.59239	-24.57507
Al		-241.89986	-241.91722	-241.92323	-241.90980
O		-74.89662	-74.93402	-74.96478	-74.95242
F		-99.49908	-99.56580	-99.60790	-99.60212
Cl		-459.57027	-459.60329	-459.65629	-459.63338
BO	$^2\Sigma$	-99.77237	-99.81701	-99.86563	-99.85647
AlO	$^2\Sigma$	-316.95027	-317.01833	-317.05586	-317.03557
BF	$^1\Sigma_g$	-124.35626	-124.42947	-124.49206	-124.47637
BCl	$^1\Sigma_g$	-484.32999	-484.37960	-484.44047	-484.40756
AlF	$^1\Sigma_g$	-341.64409	-341.72003	-341.78616	-341.77764
AlCl	$^1\Sigma_g$	-701.64726	-701.69849	-701.76868	-701.73853
O_2	$^3\Sigma_g$	-149.96714	-150.03681	-150.11869	-150.10731
F_2	$^1\Sigma_g$	-199.05115	-199.17432	-199.27478	-199.26704
Cl_2	$^1\Sigma_g$	-919.20440	-919.26990	-919.39742	-919.35776
BO_2 ($D_{\infty h}$)	$^2\Pi_g$	-174.85979	-174.94205	-175.02569	-174.99779
($C_{\infty v}$)	$^2\Pi$	-174.85624	-174.93927	-175.02858	-175.00666
AlO_2 ($D_{\infty h}$)	$^2\Pi_g$	-391.97849	-392.07773	-392.15857	-392.12772
($C_{\infty v}$)	$^2\Pi$	-391.99552	-392.07767	-392.18698	-392.16818
OBF	$^1\Sigma$	-199.51916	-199.62434	-199.73699	-199.72743
OBCl	$^1\Sigma$	-559.52565	-559.60335	-559.71723	-559.68889
OAlF	$^1\Sigma$	-416.68113	-416.78534	-416.91409	-416.90787
OAlCl	$^1\Sigma$	-776.69464	-776.77163	-776.90366	-776.87588

[a] energies in au.
[b] geometries optimized at the MP2/6-31G(d,p) level

The effect of higher angular momentum functions is obtained from a MP4SDTQ/6-311G(2df,p) calculation:

$$\Delta E(2df) = E(MP4SDTQ/6\text{-}311G(2df,p)) - E(MP4SDTQ/6\text{-}311G(d,p)) \quad (2)$$

A QCISD(T)/6-311G(d,p) computation is used to account for correlation beyond fourth order perturbation theory:

$$\Delta E(QCI) = QCISD(T)/6\text{-}311G(d,p) - E(MP4SDTQ/6\text{-}311G(d,p)) \quad (3)$$

Higher level corrections for deficiencies in the wavefunction are estimated empirically by comparing the calculated bond dissociation energy for H_2 with the exact value:

Table 2.
Structures[a] and Vibrational Frequencies[b] for AX and OAX (A = B, Al; X = O, F, Cl)

Species	$\langle S^2 \rangle$	R(AO)	R(AX)	ZPE[c]	Frequencies
BO	0.800	1.216		2.991	σ 2093
AlO	0.792	1.648		1.157	σ 810
BF			1.277	2.103	σ 1471
BCl			1.714	1.217	σ 851
AlF			1.671	1.235	σ 864
AlCl			2.135	0.681	σ 476
O_2	2.032	1.246		2.857	σ_g 1998
F_2			1.421	1.780	σ_g 1245
Cl_2			2.015	0.858	σ_g 600
BO_2 ($D_{\infty h}$)	0.932	1.259	1.259	2.885	σ_u 2351i, π_u (379, 509), σ_g 1130
($C_{\infty v}$)	0.784	1.333	1.194	5.851	π (465, 521), σ 1036, σ 2071
AlO_2 ($D_{\infty h}$)	1.155	1.644	1.644	2.115	σ_u 3720i, π_u (219, 490), σ_g 770
($C_{\infty v}$)	0.757	1.727	1.571	3.558	π (227, 234), σ 761, σ 1267
OBF		1.221	1.296	6.390	π 541, π 541, σ 1093, σ 2294
OBCl		1.221	1.683	5.417	π 441, π 441, σ 722, σ 2186
OAlF		1.626	1.644	3.696	π 238, π 238, σ 813, σ 1296
OAlCl		1.627	2.063	3.057	π 194, π 194, σ 518, σ 1232

[a] bondlengths in Ångstroms and optimized at MP2/6-31(d,p).

[b] frequencies in cm^{-1}, calculated at HF/6-31G(d,p)//HF/6-31G(d,p).

[c] zero point energies in kcal/mol; note that the ZPE's for BO_2 and AlO_2 do not include the σ_u stretching mode which has an imaginary frequency at the Hartree-Fock level.

$$\Delta E(\mathrm{HLC}) = -0.00614\, n_{\mathrm{paired}} - 0.00019\, n_{\mathrm{unpaired}}\ \mathrm{au} \tag{4}$$

where n_{paired} and n_{unpaired} are the number of electron pairs and the number of unpaired electrons, respectively. The G1 energies [7] are then obtained by combining these corrections:

$$\begin{aligned} E(\mathrm{G1}) = {} & E(\mathrm{MP4SDTQ/6\text{-}311G(d,p)}) + \Delta E(+) + \Delta E(\mathrm{2df}) + \Delta E(\mathrm{QCI}) + \Delta E(\mathrm{HLC}) \\ & + \mathrm{ZPE(HF/6\text{-}31G(d))} \end{aligned} \tag{5}$$

G2 theory [8] is an extension of the G1 method that overcomes some limitations caused by additivity assumptions. An extra calculation is performed at the MP2/6-311G(3df,2p) level:

$$\begin{aligned} E(\mathrm{G2}) = {} & E(\mathrm{G1}) + E(\mathrm{MP2/6\text{-}311G(3df,2p)}) - E(\mathrm{MP2/6\text{-}311G(2df,p)}) \\ & - E(\mathrm{MP2/6\text{-}311{+}G(d,p)}) + E(\mathrm{MP2/6\text{-}311G(d,p)}) + 0.00114\, n_{\mathrm{paired}} \end{aligned} \tag{6}$$

The correction of 0.00114 au per electron pair was determined by fitting to 55 well-established experimental atomization energies [8].

Table 3.
Bond Energies for AX and OAX (A = B, Al; X = O, F, Cl)[a]

Reaction		Bond energies in kcal/mol				
		PMP4[b]	QCISD(T)[c]	G1	G2	Exp[d]
$BF \rightarrow B + F$		174.2	168.5	181.8	180.8	179±4
$BCl \rightarrow B + Cl$		113.9	114.6	123.2	123.0	129±5
$AlF \rightarrow Al + F$		152.6	147.5	164.0	161.6	160±1
$AlCl \rightarrow Al + Cl$		110.5	111.0	122.0	120.9	119±2
$BO \rightarrow B + O$		185.0	179.8	191.7	192.0	193±4
$AlO \rightarrow Al + O$		95.4	103.7	121.5	118.9	121±2
$O_2 \rightarrow O + O$		106.3	103.0	115.3	115.6	118±0.03
$F_2 \rightarrow F + F$		31.5	25.0	37.5	36.6	37±0.1
$Cl_2 \rightarrow Cl + Cl$		39.2	38.9	58.0	55.8	57±0.001
$BO_2 \rightarrow B + 2O$	($D_{\infty h}$)	305.8	299.7	322.5	321.8	319±5
	($C_{\infty v}$)	299.6	295.0	318.0	317.1	
$AlO_2 \rightarrow Al + 2O$	($D_{\infty h}$)	177.0	181.4	212.8	209.5	216±8
	($C_{\infty v}$)	186.3	179.9	210.6	206.8	
$OBF \rightarrow B + F + O$		337.0	327.9	354.4	352.3	354±6
$OBCl \rightarrow B + Cl + O$		297.4	292.2	313.1	312.3	297±9
$OAlF \rightarrow Al + F + O$		238.3	227.4	262.5	257.4	294±4
$OAlCl \rightarrow Al + Cl + O$		202.7	195.9	223.8	221.6	249±5

[a] using MP2/6-31G(d,p) optimized geometries.
[b] with the 6-31G(d,p) basis set.
[c] with the 6-311G(d,p) basis set.
[d] using heats of formation (0 K) from the JANAF tables [14].

3. DISCUSSION

The total energies at a number of different levels of theory for the various species considered in this paper are collected in Table 1. The optimized geometries, vibrational frequencies and zero point energies are summarized in Table 2. These data are used to compute the bond energies for the diatomics and triatomics listed in Table 3; the experimental values are based on the heats of formation taken from the JANAF tables [14].

3.1 BX and AlX (X = F, Cl)

These are closed shell systems that pose no serious electronic problems. Both the G1 and G2 levels of theory are in good agreement with the experimental values for the boron monohalides; G2 theory is somewhat better for aluminum monofluoride and monochloride. The PMP4 and QCI calculations yield bond energies that are 5 - 15 kcal/mol too small.

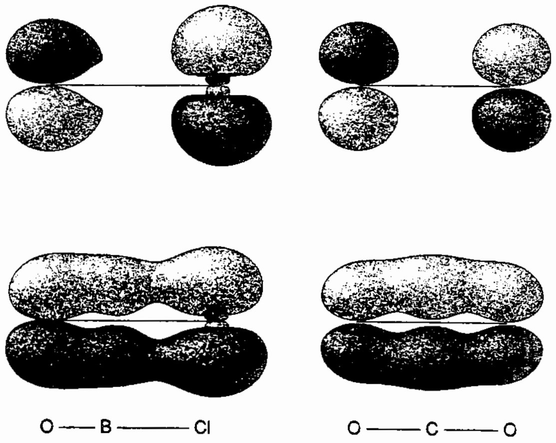

Figure 1. Comparison of the occupied π orbitals of OBCl and CO_2.

3.2 BO and AlO

The ground states of the monoxides are Σ radicals. Calculations on aluminum monoxide are troublesome because of SCF instabilities, as has been discussed in detail by Goddard et al. [5] and others [15]. The $^2\Pi$ state for AlO is 13 kcal/mol lower than the $^2\Sigma$ state at the UHF/6-31G(d,p) level, but the $^2\Sigma$ state is 10 kcal/mol lower at the QCISD(T)/6-31G(d,p) level. The bond energies computed at the G1 and G2 levels are both in good agreement with experiment. Likewise, the bond energies of O_2, F_2 and Cl_2 in good agreement with experiment at G1 and G2 levels. However, the PMP4 and QCI calculations predict values that are 5 - 20 kcal/mol too small.

3.3 BO_2 and AlO_2

The dioxides of boron and aluminum are $^2\Pi_g$ radicals of $D_{\infty h}$ symmetry, but single reference electronic structure calculations encounter serious problems. Like the monoxide, the ground state of AlO_2 is SCF unstable. Goddard et al. [5] and others [16] have discussed this problem in greater detail and have examined a number of different bonding arrangements for these molecules. In addition to the SCF stability problems, single reference determinant calculations for BO_2 and AlO_2 suffer from spatial symmetry breaking in the wavefunctions.

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Table 4.
Heats of Formation of AX and OAX (A = B, Al; X = O, F, Cl)[a]

Species	ΔH_f^o (0) in kcal/mol				
	PMP4[b]	QCISD(T)[c]	G1	G2	Exp[d]
B(g)	-	-	-	-	133±3
Al(g)	-	-	-	-	78±1
O	53.1	51.5	57.7	57.8	58.98±0.02
F	15.7	12.5	18.7	18.3	18.5±0.1
Cl	19.6	19.4	29.0	27.9	28.590±0.001
BO	0.8	4.4	-1.4	-1.6	1±2
AlO	36.0	26.1	14.4	17.2	16±2
BF	-25.8	-23.4	-30.5	-29.9	-28±3
BCl	38.3	37.5	38.5	37.6	33±4
AlF	-58.6	-56.8	-67.1	-65.1	-63.5±0.8
AlCl	-12.6	-13.3	-14.8	-14.7	-12±2
BO_2 ($D_{\infty h}$)	-65.9	-64.1	-74.6	-73.6	-68±2
AlO_2 ($D_{\infty h}$)	7.4	-0.2	-19.2	-15.8	-20±8
OBF	-135.5	-131.3	-145.3	-143.6	-144±3
OBCl	-92.0	-88.61	-93.8	-94.0	-76±7
OAlF	-91.2	-85.2	-107.9	-103.1	-138±4
OAlCl	-51.7	-46.7	-58.9	-57.7	-83±5

[a] MP2/6-31G(d,p) geometries.
[b] with the 6-31G(d,p) basis set.
[c] with the 6-311G(d,p) basis set.
[d] from the JANAF tables [14].

Electron correlation energies for BO_2 and AlO_2 were calculated at both the $C_{\infty v}$, broken symmetry geometry and at the symmetric $D_{\infty h}$ structure (with a symmetry constrained wavefunction). The MPn calculations are lower for $C_{\infty v}$ species; however, the QCI, G1 and G2 energies are lower for symmetric $D_{\infty h}$ structures by 2 - 5 kcal/mol. Both of the G1 and G2 results for BO_2 are in good agreement with experiment. The Hartree-Fock wavefunction for $D_{\infty h}$ AlO_2 is internally unstable and optimizes to a lower energy C_{2v} structure (R(AlO) = 1.723 Å, ∠OAlO = 120.6°); however, partial optimization at the MP2 level leads back toward the $D_{\infty h}$ structure. The G1 and G2 calculated bond energies for the AlO_2 are 3 - 6 kcal/mol lower than experiment. A substantial fraction of this discrepancy is probably due to the broken symmetry in the AlO_2 calculation; however, the large error bars on the experimental value should not go unnoticed.

3.4 OBX and OAlX (X = F, Cl)

These species are closed shell singlets and should pose no special electronic problems. The valence shells of these molecules are isoelectronic with CO_2 and have the same type of π orbitals as CO_2 (Fig. 1). The G1 and G2 bond energies for OBF are both in good agreement with experiment, as could be anticipated from the good agreement obtained for the various reactions discussed above. However, the bond energy for OBCl is calculated to be 15 kcal/mol greater than obtained from the experimental heats of formation. This discrepancy is well outside the ±2 or ±3 kcal/mol range seen for the other bond energies. The inescapable conclusion is that *the experimental heat of formation of OBCl is in error and needs to be re-examined.* The problems are even more pronounced for OAlF and OAlCl, where the calculated bond energies are 25 to 35 kcal/mol lower than experiment. Because of the good agreement obtained for the bond dissociation energies for the other aluminum species, one must conclude that *the experimental heats of formation of OAlF and OAlCl are in error and should be re-investigated.*

4. CONCLUSIONS

Table 4 gives heats of formation derived from the bond energies given in Table 3. The G1 and G2 levels of theory in good agreement with experiment for most species. The major exceptions are OBCl, OAlF and OAlCl. OBCl is calculated to be more stable by 15 kcal/mol, OAlF and OAlCl are found to be less stable by 37 and 28 kcal/mol, respectively. Both $AlF + O_2 \rightarrow OAlF + O$ and $AlCl + O_2 \rightarrow OAlCl + O$ are calculated to be endothermic, contrary to what was previously thought. Since these reactions do occur, this suggests that they proceed by a different mechanism than the boron analogues and yield products other than OAlX + O (X = F, Cl). We are currently mapping out the detailed mechanism and energetics of all 4 reactions [6].

5. ACKNOWLEDGEMENTS

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