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Ab initio molecular orbital calculations of the mechanism of oxidation of boron and aluminum monohalides

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Abstract

The mechanisms of BF, BCl, AlF and AlCl reacting with $^3\text{O}_2$ have been investigated by ab initio molecular orbital methods at the PMP4/6-31G^{*} and G2 levels of theory. The $\text{BX} + ^3\text{O}_2$ reactions proceed via an XBOO intermediate that can dissociate to give $\text{XBO} + ^3\text{O}$, which can react further to yield $\text{BO}_2 + \text{X}$. At the G2 level of theory, the initial barrier for $\text{BCl} + ^3\text{O}_2$ is 8.5 kcal/mol and for $\text{BF} + ^3\text{O}_2$ is 12.4 kcal/mol. These compare very favorably with the experimental barriers of 6.5 and 12 kcal/mol, obtained by fitting model transition states to the observed rate data. For $\text{AlX} + ^3\text{O}_2$, the barrier for $\text{XAlOO} \rightarrow \text{XAlO} + ^3\text{O}$ is much higher than the barrier for decomposition back to reactants, and the reaction may proceed by a different mechanism.

1. Introduction

Boron and aluminum clusters are possible additives to increase the energy density of solid fuel propellants [1–3]. Boron and aluminum monohalides are key intermediates in these oxidation process. Rate constants have been measured for BF, BCl and AlCl reacting with a number of different oxygen donating species over a wide temperature range [1,4–11]. 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 [1]. The reactions of B, BO, Al and AlO

with various oxidants have also been studied experimentally [1–11] and theoretically [12–14]. Most closely related to the present work is a study by Marshall and Goddard and co-workers [13] in which high level ab initio molecular orbital theory was used to examine the reactions of B and Al with O_2 and CO_2 .

In an earlier paper [12], we used ab initio molecular orbital calculations at the G2 level of theory to obtain bond dissociation energies and heats of formation of BX, AlX, OBX and OAlX (X = O, F, Cl). Except for OBCl, OAlF and OAlCl, the G2 theory give results that are very good agreement with the experimental heats of formation (average absolute deviation of 2.8 kcal/mol). However OBCl was calculated to be 18 kcal/mol more stable than experiment; OAlF and OAlCl were calculated to be 35 and 25 kcal/mol less stable than experiment. These discrepancies are well outside the ± 2 kcal/mol

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Table 1
Optimized geometries ^a of transition states and intermediates for BX + ³O₂

System	State	BX	BO ₁	BO ₂	O ₁ O ₂	∠XBO ₁	∠XBO ₂	∠BO ₁ O ₂
BCl + ³ O ₂	TS1	1.7138	1.9448		1.2109	102.66		125.11
	MN1	1.7188	1.3876		1.3598	118.47		110.68
	TS2	1.6965	1.2711		1.5380	110.68		110.89
	TS3(A')	1.7034	1.2304	1.7401		156.99	103.99	
	TS3(A'')	1.6977	1.2411	1.9167		159.69	112.73	
	MN2(B ₂)	1.7460	1.3636	1.3636		118.30	118.30	
	MN2(A')	1.7377	1.3489	1.4061		115.89	124.78	
	TS4(A')	2.2108	1.2331	1.3378		85.33	105.70	
	TS4(A'')	2.0607	1.2457	1.3639		83.93	120.66	
BF + ³ O ₂	TS1	1.2860	1.8824		1.2208	101.99		123.84
	MN1	1.3136	1.3986		1.3549	116.74		110.52
	TS2	1.3115	1.2754		1.5716	141.09		109.46
	TS3(A')	1.3035	1.2363	1.7347		157.98	103.91	
	TS3(A'')	1.3031	1.2384	1.9317		162.47	108.30	
	MN2(B ₂)	1.3298	1.3759	1.3759		119.23	119.23	
	MN2(A')	1.3256	1.3565	1.4066		120.76	123.83	
	TS4(A')	2.0993	1.2277	1.3427		85.20	100.31	
	TS4(A'')	2.0079	1.2348	1.3483		79.16	111.52	

^a Bond lengths in Å and angles in deg, optimized at the MP2/6-31G* level; all structures are planar.

average absolute error range found when comparing G2 calculations with well established experimental values and suggest that the experimental heats of

formation for OBCl, OAlF and OAlCl are in error and need to be re-examined. Others have reached similar conclusions [15]. In the present paper we use

Table 2
Frequencies of transition states and intermediates for BX + ³O₂ ^a

System	State	Frequencies
BCl + ³ O ₂	TS1	A' 1277i, A'' 87, A' 168, A' 358, A' 883, A' 1397
	MN1	A' 179, A' 268, A' 397, A' 919, A' 1174, A' 1234
	TS2	A' 2281i, A'' 223, A' 276, A' 444, A' 781, A' 1504
	TS3(A')	A' 2201i, A' 245, A' 290, A'' 389, A' 683, A' 1535
	TS3(A'')	A' 2511i, A' 234, A' 406, A'' 419, A' 709, A' 1852
	MN2(B ₂)	A ₁ 288, B ₂ 356, B ₁ 561, A ₁ 712, B ₂ 1164, A ₁ 1421
	MN2(A')	A' 302, A' 350, A'' 535, A' 679, A' 1200, A' 1389
	TS4(A')	A' 678i, A' 188, A' 322, A'' 487, A' 1002, A' 1568
	TS4(A'')	A' 1004i, A' 277, A' 422, A'' 455, A' 889, A' 1788
BF + ³ O ₂	TS1	A' 1528i, A'' 95, A' 229, A' 381, A' 1313, A' 1399
	MN1	A' 197, A' 311, A' 491, A' 1112, A' 1208, A' 1340
	TS2	A' 2429i, A'' 264, A' 335, A' 553, A' 852, A' 1635
	TS3(A')	A' 2454i, A' 302, A' 430, A'' 574, A' 939, A' 1731
	TS3(A'')	A' 453i, A' 244, A' 454, A'' 493, A' 1000, A' 1995
	MN2(B ₂)	A ₁ 402, B ₂ 414, B ₁ 646, A ₁ 880, B ₂ 1414, A ₁ 1427
	MN2(A')	A' 350, A' 454, A'' 614, A' 866, A' 1358, A' 1494
	TS4(A')	A' 214i, A' 160, A' 438, A'' 486, A' 976, A' 2541
	TS4(A'')	A' 470i, A' 2224, A' 442, A'' 466, A' 957, A' 2202

^a Frequencies in cm⁻¹ calculated at the MP3/6-31G* level.

ab initio molecular orbital calculations to explore the mechanism for the reaction of ${}^3\text{O}_2$ with BF, BCl, AlF and AlCl.

2. Method

All electronic structure calculations were carried out using the GAUSSIAN 92 [16] systems of programs. Restricted Hartree–Fock was used for closed shell species and unrestricted for open shell. Equilibrium geometries were optimized with the 6-31G* basis set [17–20] at the Hartree–Fock level (HF/6-31G*) and at the second-order Møller–Plesset perturbation theory level (MP2/6-31G*). Vibrational frequencies and zero-point energies were calculated at both the HF/6-31G* level and the MP2/6-31G* level using the HF and MP2 optimized geometries, respectively. Total energies were calculated by fourth-order Møller–Plesset perturbation theory, using MP2 optimized geometries, with an approximate spin projection method [21,22] to correct for spin contamination in the open shell systems (PMP4/6-31G*//MP2/6-31G*, frozen core). More accurate estimates of the total energies for two of the barriers were obtained using the G2 level of theory [23].

3. Results and discussion

Table 1 lists the optimized geometries of the transition structures and intermediates for the oxidation reaction of $\text{BCl} + {}^3\text{O}_2$; the corresponding data for the reactants and products have been published previously [12]. A total of four types of transition states were located, labeled TS1 to TS4, and two types of intermediate minima were found, MN1 and MN2. All structures are planar and, in general, the geometries obtained with the HF/6-31G* and MP2/6-31G* levels of theory are quite similar. The MP2/6-31G* vibrational frequencies are listed in Table 2. The HF and MP2 frequencies are quite similar, except for the imaginary frequencies, which tend to be larger in magnitude at the MP2 level.

The reaction mechanism for $\text{BCl} + {}^3\text{O}_2$ is shown in Fig. 1a. The energies in the diagram were calculated at the MP4SDTQ/6-31G* level with spin projection, using the MP2/6-31G* optimized ge-

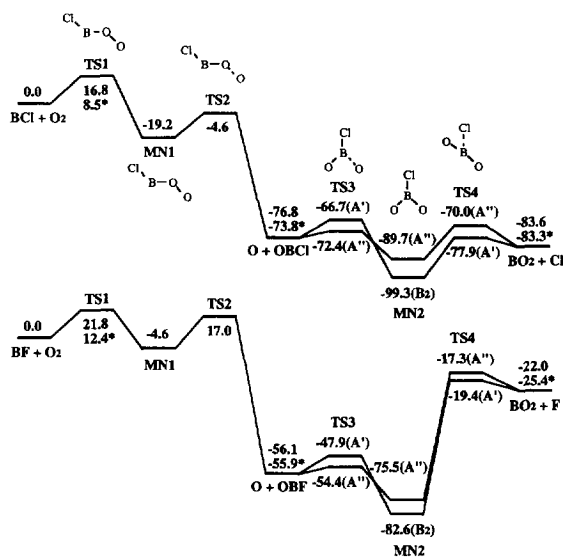
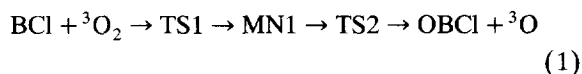
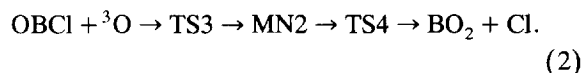


Fig. 1. Energies of the transition states and intermediates for $\text{BX} + {}^3\text{O}_2$ computed at the PMP4/6-31G* level (no superscript) and the G2 level of theory (asterisk).

ometries. Corrections for zero-point energy are added in these energies using the MP2 frequencies without scaling. MP2 calculations on BO_2 suffer from artificial symmetry breaking [12,13]; at the G2 level, the $D_{\infty h}$ structure of BO_2 is about 4.7 kcal/mol lower than the C_{2v} structure [12]. Intrinsic reaction coordinate (IRC) following [24,25] has been used to characterize all transition states. These calculations confirm that TS1 connects the reactants and intermediate MN1, and TS2 connects MN1 and the products $\text{O} + \text{OBCl}$. No transition state has been found which directly connects reactants to products $\text{O} + \text{OBCl}$ or $\text{BO}_2 + \text{Cl}$. No minimum was evident for a closed-ring structure for ClBO_2 (in the case of dioxirane, such a structure is ≈ 12 kcal/mol lower [26]). The only channel for the formation of $\text{BO}_2 + \text{Cl}$ from $\text{BCl} + {}^3\text{O}_2$ appears to be through $\text{O} + \text{OBCl}$ with two transition states and one intermediate. From this study the reaction mechanism can be written as



and



Since unpaired electrons of oxygen and $\text{BO}_2 + \text{Cl}$ can be either both in-plane or one in plane and the other out-of-plane, both A' and A'' states are permitted in Eq. (2). For the A' surface the barrier height for $\text{O} + \text{OBCl}$ going to MN2 is 11.1 kcal/mol and 3.7 kcal/mol for $\text{BO}_2 + \text{Cl}$ to MN2 , while for the A'' surface the first barrier is only 4.4 kcal/mol and the second is 13.6 kcal/mol (from $\text{O} + \text{OBCl}$ to $\text{TS4}(A'')$). By contrast, only the A'' state is symmetry allowed in Eq. (1). Because TS1 is higher than reactants and all the other transition states are significantly lower than reactants, the reaction dynamics is dominated by TS1 .

The reaction energy diagram for $\text{BF} + {}^3\text{O}_2$ is present in Fig. 1b. This diagram is quite similar to the one for $\text{BCl} + {}^3\text{O}_2$, except TS2 is higher than the reactants and closer to TS1 . Optimized structures for the transition states and minima are given in Table 1 and the calculated harmonic frequencies are listed in Table 2.

While the $\text{PMP4}/6\text{-}31\text{G}^*$ level of theory is useful for exploring the mechanism of these reactions, a higher level of theory is needed for more reliable barrier heights. The G2 level of theory [23] is expected to be accurate to within ± 2 kcal/mol. For TS1 , the barrier heights calculated at the G2 level are 8.5 kcal/mol for $\text{BCl} + {}^3\text{O}_2$ and 12.4 kcal/mol for $\text{BF} + {}^3\text{O}_2$. When the experimental rate constants are fitted to a model transition state [10], a barrier height of 7.4 kcal/mol is obtained for $\text{BCl} + {}^3\text{O}_2$. If the geometry and vibrational frequencies computed in

the present work are used to model the transition state, a barrier height of ≈ 6.5 kcal/mol is obtained. For the $\text{BF} + {}^3\text{O}_2$ rates, this approach yields a barrier height of ≈ 12 kcal/mol. Thus, the barriers computed at the G2 level of theory are in good agreement with the barrier heights obtained from experiment by model transition state theory calculations.

The A'' TS3 transition state for BFO_2 has two SCF wave functions with different energies that are both stable with respect to perturbations involving single excitations. The energy difference between these two states is only 0.1 kcal/mol. For such small energy differences, allowed or avoided state crossings may occur. No evidence of a crossing was found during the MP2 optimization of $\text{TS3}(A'')$, but MCSCF calculations may reveal more details about the surface.

Optimized geometries for the reactions of $\text{AlCl} + {}^3\text{O}_2$ and $\text{AlF} + {}^3\text{O}_2$ are given in Table 3. The energies of the transition states and intermediates are shown in Fig. 2 and the vibrational frequencies are listed in Table 4. Structure MN1 could not be found at the MP2 level because of an apparent state crossing in this region. No true transition states have been found in the region between $\text{OAlX} + \text{O}$ and $\text{AlO}_2 + \text{X}$ ($\text{X} = \text{Cl}, \text{F}$). Reaction path following at the Hartree–Fock level showed that TS1 and TS2 for $\text{AlCl} + {}^3\text{O}_2$ connect reactants to MN1 and MN1 to products $\text{OAlCl} + \text{O}$, respectively. The state crossings and symmetry breaking found in the $\text{AlX} + {}^3\text{O}_2$ systems suggests that multiconfiguration SCF (MC -

Table 3
Optimized geometries^a of transition states and intermediates for $\text{AlX} + {}^3\text{O}_2$

System	State	AlX	AlO ₁	AlO ₂	O ₁ O ₂	$\angle \text{XAlO}_1$	$\angle \text{XAlO}_2$	$\angle \text{AlO}_1\text{O}_2$
$\text{AlCl} + {}^3\text{O}_2$	TS1	2.1211	2.1012		1.2318	96.59		128.14
	MN1 ^b	2.1040	1.7605		1.3289	112.59		110.38
	TS2	2.0953	1.7586		2.1684	115.36		96.54
	MN2(B ₂)	2.0651	1.7515	1.7515		120.61	120.61	
	MN2(A'')	2.0658	1.7463	1.7617		118.05	123.96	
$\text{AlF} + {}^3\text{O}_2$	TS1	1.6664	2.0937		1.2365	96.31		126.78
	MN1 ^b	1.6336	1.7625		1.3275	112.73		110.53
	TS2	1.6606	1.7614		2.2218	116.76		96.40
	MN2(B ₂)	1.6464	1.7467	1.7467		120.34	120.34	
	MN2(A'')	1.6469	1.7467	1.7599		118.10	123.03	

^a Bond lengths in Å, angles in deg, optimized at the $\text{MP2}/6\text{-}31\text{G}^*$ level; all structures are planar.

^b Optimized at the $\text{HF}/6\text{-}31\text{G}^*$ level.

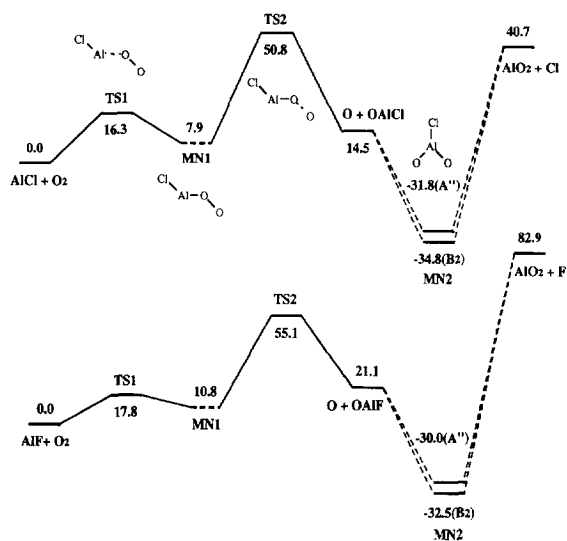


Fig. 2. Energies of the transition states and intermediates for $\text{AlX} + {}^3\text{O}_2$ computed at the PMP4/6-31G* level of theory.

SCF) calculations may be needed for some of the structures; however, this is beyond the scope of the present study.

Comparison of the $\text{AlX} + \text{O}_2$ barrier heights with experiment is complicated by the difficulties in the electronic structure calculations. If MN1 reacts further by some alternate, low energy route, then TS1 could be rate limiting. At the PMP4/6-31G* level, the calculated barriers for $\text{AlX} + {}^3\text{O}_2$ are similar to $\text{BCl} + {}^3\text{O}_2$; comparison with the G2 calculations on $\text{BCl} + {}^3\text{O}_2$ suggests barriers for $\text{AlX} + {}^3\text{O}_2$ may be 6–10 kcal/mol at higher levels of theory (e.g. MRCI

calculations with large basis sets). This would be consistent with the observed rates [8,11]. However, the experimental data indicate there may be two competing pathways [8,11]. Further theoretical studies on this system may be warranted.

4. Conclusions

The PMP4SDTQ/6-31G(d, p)//MP2/6-31G(d, p) level of theory has been used to map out the mechanism and energetics of oxidation reactions of boron and aluminum monohalides. For the reactions of $\text{BX} + {}^3\text{O}_2$ ($\text{X} = \text{F}, \text{Cl}$), there is no reaction channel which directly forms $\text{BO}_2 + \text{X}$. The reaction proceeds first to $\text{OBX} + \text{O}$ then to $\text{BO}_2 + \text{X}$. The initial barrier heights (energy difference between TS1 and reactants) for these reactions are 16.8 and 21.8 kcal/mol for $\text{BCl} + {}^3\text{O}_2$ and $\text{BF} + {}^3\text{O}_2$, respectively, at the PMP4/6-31G* level. The more accurate G2 calculations show the initial barrier heights are 8.5 and 12.4 kcal/mol, respectively, and are in good agreement with experimental estimates of the barrier heights.

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Table 4

Frequencies of transition states and intermediates for $\text{AlX} + {}^3\text{O}_2$ ^a

System	State	Frequencies
$\text{AlCl} + {}^3\text{O}_2$	TS1	A' 2349i, A' 76, A' 113, A' 294, A' 513, A' 797
	MN1 ^b	A'' 77, A' 145, A' 221, A' 540, A' 768, A' 1213
	TS2	A' 107i, A' 54, A' 100, A' 219, A' 530, A' 794
	MN2(B ₂)	B ₂ 171, A ₁ 206, B ₁ 246, A ₁ 519, A ₁ 802, B ₂ 897
	MN2(A'')	A' 182, A' 215, A' 243, A' 516, A' 800, A' 894
$\text{AlF} + {}^3\text{O}_2$	TS1	A' 2083i, A' 79, A' 143, A' 296, A' 789, A' 882
	MN1 ^b	A' 81, A' 172, A' 259, A' 740, A' 926, A' 1220
	TS2	A' 95i, A' 60, A' 111, A' 261, A' 736, A' 905
	MN2(B ₂)	B ₂ 219, A ₁ 235, B ₁ 279, A ₁ 677, B ₂ 903, A ₁ 965
	MN2(A')	A' 224, A' 252, A' 274, A' 673, A' 901, A' 964

^a Frequencies in cm^{-1} calculated at the MP3/6-31G* level of theory.

^b Computed at the HF/6-31G* level of theory.

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