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Reactions of boron and aluminum atoms with small molecules

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Abstract

The reactions of B and Al atoms with O₂ and CO₂ have been investigated at unrestricted Hartree-Fock and many body perturbation (UMP2 and UMP4) levels of theory, with 6-31G* and larger basis sets. The status of *ab initio* studies of these radicals is discussed. Interesting difficulties arise due to Hartree-Fock instabilities and symmetry breakings for certain of the BO₂ and AlO₂ species. The predicted vibrational spectra of two isomers of AlCO₂ are in good agreement with recent matrix isolation studies of these complexes. Reactions with O₂ and CO₂ are calculated to proceed via formation of excited adducts which either may be stabilized collisionally or may dissociate further to products. A number of the intermediates and transition states have been characterized. The results are combined with the quantum RRR model to predict the kinetic parameters, which are compared with experimental results where these are available.

1. INTRODUCTION

Oxidation of aluminum and boron forms an important part of the chemistry of advanced solid propellants, as discussed elsewhere in this volume^{1,2}. The need for reliable kinetic information to model propellant combustion has provided an impetus for several experimental studies of aluminum and boron reactivity^{1,3}. In order to understand the experimental results in terms of the fundamental potential energy surfaces involved, and to permit estimation of kinetic data for systems where few or no kinetic measurements have been made, we have begun *ab initio* computational investigations of the chemistry of aluminum and boron oxidation.

As a first step we focus on atomic B and Al and the formation of mono- and dioxides, and of addition products with CO₂. While there have been several previous theoretical investigations of small B and Al oxides they have been concerned mainly with structural and spectroscopic aspects, and there has been little focus on thermochemistry and

the implications of the *ab initio* results for the kinetics of the formation and reactivity of these oxides. Here we derive bond energies, rate constants and branching ratios. Experimental data is available for some of the systems studied, which permits assessment of the accuracy of the theoretical methods employed.

2. THEORETICAL APPROACH

2.1 Quantum Chemical Calculations

All quantum chemical computations were carried out with the GAUSSIAN88 or GAUSSIAN90 program systems^{4,5}. The split valence plus polarization 6-31G* basis and this set supplemented by diffuse sp functions, 6-31+G*, were used for most of the theoretical work. The unrestricted Hartree-Fock (UHF) method was employed and spin contamination monitored by the values of $\langle S^2 \rangle$. All geometries were optimized fully at the UHF level employing energy gradient based procedures. In addition, for certain key species structures were refined further through geometry optimization at a level including electron correlation, second order Møller-Plesset perturbation theory (UMP2). The natures of all stationary points, i.e. minima or transition states, were verified by computing the harmonic vibrational frequencies at the UHF or UMP2 levels. These predicted vibrational frequencies were scaled⁶ by 0.90 UHF or 0.95 UMP2 and used in the computation of zero point vibrational energies (ZPEs). Higher level single point energies at the UHF and/or UMP2 geometries were determined at the UMP4 level (UMP4SDTQ) and for a few structures with the quadratic configuration interaction method⁷ (QCISD(T)). Spin projected values⁸ of the UMP4 energies (PMP4) were considered whenever $\langle S^2 \rangle$ deviated significantly from ideal values.

The possible existence of Hartree-Fock instabilities⁹ in the UHF wavefunctions was tested for most of the molecules. Internal instabilities were noted for AlO and certain electronic states and geometries of BO₂, AlO₂ and BCO₂. Some reoptimizations of the UHF wavefunctions with the release of constraints were performed. In addition, certain molecules, most notably OBO and OAlO, broke symmetry from $D_{\infty h}$ to $C_{\infty v}$ and the geometries were redetermined in the lower point group. These symmetry breakings have been noted previously^{10,11} in similar studies. A clear resolution of the difficulties probably will require a more flexible multireference wavefunction.

2.2 Kinetic Analysis

As discussed below, it seems likely that the reactions considered here proceed via formation of intermediate complexes, which may decompose back to the original reactants, fragment to new products or be stabilized collisionally. The elementary steps may be summarized as

We have used information about the potential energy surface (PES) to determine the

kinetics by means of the quantum RRRK (QRRK) model, as described by Dean¹² and Westmoreland.^{13,14} The reactants $A + B$ collide to form an initially excited adduct AB^* with rate constant k_f . We calculate k_f by transition state theory¹⁵ (TST) if there is a well-defined energy barrier between $A + B$ and AB . If there is no clear barrier, then we determine k_f by consideration of the passage of the reactants over the centrifugal barrier in the long range attractive potential between them.¹⁶ The potential is defined by $V(r) = -C_6/r^6$ where C_6 may be estimated from the polarizabilities of the reactants A and B .¹⁷ This approximate treatment will be appropriate if there is only a weak interaction between the approaching reactants in the region of the barrier. The adduct is initially excited by the energy released in the formation of new bonds during addition, and may undergo one of three processes:

(1) The excited adduct AB^* may be collisionally stabilized by exchanging energy with the bath gas, which here is always taken to be argon for compatibility with laboratory data. The effective first order collisional stabilization rate constant is taken to be $\beta k_s[Ar]$ where β is Troe's collisional efficiency factor,¹⁸ which decreases from 0.40 at 298 K to 0.11 at 2000 K for Ar, and k_s is the Lennard-Jones collision rate constant.¹²

(2) AB^* may decompose back to the reactants $A + B$ with a first order rate constant $k_b(E)$, which depends on the internal energy E of the adduct. One weakness of typical applications of QRRK is that they do not take account of the temperature dependence of the pre-exponential factor for k_b , A_b , so here we have calculated A_b at each temperature investigated. If there is a well-defined barrier to decomposition then A_b may be deduced from TST. If there is no well-defined barrier to decomposition of the adduct we have assumed instead an overall activation energy for k_b equal to the well-depth of AB relative to $A + B$, E_0 , and derived A_b by setting the ratio $k_f/\{A_b \exp(-E_0/RT)\}$ equal to the equilibrium constant for $A + B \rightleftharpoons AB$ at each temperature. A more exact treatment would derive the energy of the transition state relative to AB by means of variational TST.¹⁹

(3) AB^* may decompose to new products $C + D$ with an energy-dependent rate constant $k_p(E)$, which is analyzed analogously to $k_b(E)$.

In some cases the excited adduct AB^* may also isomerize to a new excited species, which in turn may isomerize back to AB^* , fragment to products or be stabilized collisionally. Total rate constants for formation of AB , $C + D$ and so on are found by summing the energy-dependent elementary rate constants of equation (1) over all values of E , weighted by the relative E distributions. The QRRK approach calculates this distribution using the geometric mean frequency $\bar{\nu}$ of the adduct.¹²

We recognize some weaknesses of the QRRK model. First, angular momentum is taken properly into account only in the high-pressure limit, via the pre-exponential A factors for decomposition of the adduct. Thus no discrimination is made between inactive and active rotational modes of a dissociating molecule. Rotational energy in the active mode is available for crossing barriers to dissociation, so that QRRK falloff curves are, in principle, inaccurate.

Second, the QRRK method requires treatment of a hindered internal rotation as a low-frequency vibration, which may be a satisfactory approximation at room temperature but is certainly poor at combustion temperatures. Fortunately this error will tend to cancel when ratios of partition functions are considered, e.g. for the estimation of the A factors.

Third, the internal energy of the adduct is artificially quantized in units of $h\bar{\nu}$, which imposes an energy resolution of typically 5 kJ mol⁻¹ on the systems analyzed here. Thus,

there is a significant uncertainty in any energy barriers derived from QRRK fits to experimental data. In practice, this limitation of QRRK is not usually severe because this energy resolution is still smaller than the uncertainties in almost all experimental and *ab initio* relative energies. Despite these disadvantages, QRRK has often showed good agreement with experiment,¹³ and is appropriate given the uncertainties in several of the input parameters (see Sec. 5). Future RRKM¹⁹ calculations are planned to test the effect of some of these approximations in QRRK in more detail.

3. THEORETICAL PREDICTIONS OF STRUCTURES AND VIBRATIONAL FREQUENCIES

3.1 The Diatomic Molecules BO and AlO

Both the BO and AlO radicals have been well studied experimentally by electronic²⁰ and microwave^{21,22} spectroscopy. In its $^2\Sigma^+$ ground electronic state, BO has an equilibrium bond length (r_e) of 1.2049 Å and a vibrational frequency (ω_e) of 1885.69 cm^{-1} .^{20,21} Experimentally the AlO ground electronic state has r_e equal to 1.6179 Å and a ω_e of 979.23 cm^{-1} .^{20,22} *Ab initio* theoretical work on these diatomic radicals allows comparisons with experiment and thus some assessment of the probable reliabilities of the predictions on much less well known species such as AlO_2 , BCO_2 , and AlCO_2 .

The theoretical predictions for BO are consistent with the trends observed for numerous small molecules.⁶ At the UHF/6-31G* level a bond distance of 1.187 Å is predicted which is 0.018 Å less than experiment. Electron correlation at the UMP2/6-31G* level yields an equilibrium bond length of 1.217 Å slightly longer than the experimental value. A higher level UMP3/6-31G* result⁶ is 1.204 Å, in excellent agreement with experiment. The UHF/6-31G* vibrational frequency of BO is determined to be 2093 cm^{-1} . This value is then scaled by a factor of 0.90, which is commonly done with Hartree-Fock harmonic vibrational frequencies to approximately correct for anharmonicity and restriction to the SCF level of theory. Thus the scaled result for BO is a vibrational frequency of 1884 cm^{-1} . Spin contamination was moderate with $\langle S^2 \rangle$ equal to 0.80. No real changes were observed if the UHF/6-31+G* level was employed for BO as the bond length remained identical to the UHF/6-31G* result to three decimal places and the vibrational frequency decreased by 10 cm^{-1} .

A quartet state of BO also was considered theoretically. The geometry optimized quartet BO was $\sim 570 \text{ kJ mol}^{-1}$ above the ground state doublet molecule at the UMP4/6-31+G* level. The UHF/6-31+G* quartet bond length was 1.393 Å or $\sim 17\%$ greater than in the ground state. The predicted vibrational frequency for quartet BO is 1278 cm^{-1} UHF/6-31+G* or 1150 cm^{-1} if scaled. Quartet electronic states of the BO radical do not appear to have been characterized experimentally.

The theoretical treatment of the AlO radical proved considerably more difficult. Several electronic configurations which may be viewed as corresponding to Al^0O^0 , Al^+O^- , and $\text{Al}^{2+}\text{O}^{2-}$ contribute significantly to the wavefunction in the region of the equilibrium bond length.²³ Only rather extensive complete active space multiconfiguration self-consistent-field (CASSCF) calculations²³ have yielded very good results in comparison with experiment for AlO. In the present work, we have focused on one-configuration methods (UHF) and on electron correlation schemes starting from a single reference such as UMP2

or UMP4. The UHF/6-31G* theoretical level predicts an AlO bond length of 1.697 Å which is a full 0.08 Å greater than the well known experimental result. The predicted vibrational frequency is 809 cm⁻¹ with this method or 728 cm⁻¹ if scaled in the usual way. However, the experimental vibrational frequency, ω_e , is 978 cm⁻¹. Neither the bond length nor the vibrational frequency is typical of SCF theory with a split valence plus polarization basis. Moreover, spin contamination does not seem an overly serious problem as $\langle S^2 \rangle$ is 0.79. Pointwise geometry optimization of AlO at the more elaborate UCISD/6-31G* and QCISD(T)/6-311+G* levels gave somewhat better bond lengths of approximately 1.66 and 1.65 Å respectively. Caution is required in considering these correlated level results due to the unusual bond length result with the UHF starting wavefunction.

In fact, testing the UHF wavefunction for AlO at the optimum geometry for Hartree-Fock instabilities⁹ indicates the wavefunction to be unstable. Reoptimization of the UHF wavefunction at $r = 1.697$ Å results in an increase in $\langle S^2 \rangle$ to 0.83 and a *lowering* of the total energy from -316.72218 a.u. (UHF) to -316.74068 a.u. (stable) (1 a.u. $\approx$ 2625 kJ mol⁻¹). One view of such Hartree-Fock instabilities relates them to the need for a flexible wavefunction capable of describing degenerate correlation.²⁴ There is no improvement in the UHF results for AlO with extension of the basis set to 6-31+G*. Møller-Plesset results for AlO also are problematic due to the UHF instability. For example, the UMP4 energies with the stable reoptimized UHF wavefunction were higher than with the ordinary UHF starting point.

These results on ground state AlO are somewhat disappointing as this molecule is a key product of two of the gas phase radical reactions of interest, Al + O₂ and Al + CO₂. Some uncertainty is introduced into the energetics of AlO by our inability to predict the AlO bond length and vibrational frequency accurately. However, only computationally intensive (and expensive) large scale MCSCF calculations are likely to correct this problem fully. In the absence of such computations we have relied on a mix of theoretical and experimental results for AlO.

For comparison with BO the lowest quartet electronic state of AlO also was examined. At the UMP4/6-31+G* level and the SCF geometries, the quartet state lies adiabatically ~ 300 kJ mol⁻¹ above the ground state of AlO. The optimized bond length in this excited state is predicted to be 1.775 Å (UHF/6-31+G*). The predicted vibrational frequency is 761 cm⁻¹ or 685 cm⁻¹ if scaled. These values stand as plausible initial predictions for two of the molecular constants of this experimentally unexamined quartet electronic state of AlO.

3.2 Minimum Energy Structures for BO₂ and AlO₂

The BO₂ radical is known experimentally^{25,26,27,28} to be a linear species of D_{∞h} symmetry with a bond length of 1.265 Å and vibrational frequencies: ν_1 1070 cm⁻¹, ν_2 464 cm⁻¹, and ν_3 1278.26 cm⁻¹. Its electronic spectrum has been examined at ever increasing resolution over the past three decades as an important example of a Renner-Teller molecule. We have employed four levels of theory UHF/6-31G*, UMP2/6-31G*, UHF/6-31+G*, and UMP2/6-31+G* to predict the geometries and vibrational frequencies of OBO. In addition, a BOO species of C_{∞v} symmetry was studied as were several possible bent electronically excited states of OBO.

At all four theoretical levels considered, the harmonic vibrational frequencies of D_{∞h} OBO included a single large imaginary value for an asymmetric stretch. Motion along this

Figure 1. Optimized structures for BOO and OBO in $C_{\infty v}$ and $D_{\infty h}$ symmetries. Four levels of theory were employed: UHF/6-31G*, UMP2/6-31G*, UHF/6-31+G*, and UMP2/6-31+G*.

normal coordinate leads to an OBO species of $C_{\infty v}$ symmetry with the BO bonds of significantly different lengths. In Fig. 1, although the predicted bond lengths for a $D_{\infty h}$ BO_2 species of 1.254 to 1.261 Å are in reasonable agreement with the experimental value of 1.265 Å, it must be recalled that the theoretical structures are *not* minima. In $C_{\infty v}$, at the UHF level the two BO bonds differ in length by ~ 0.14 Å which is reduced to ~ 0.12 Å at the UMP2 level. Normally reasonably reliable theoretical methods, UHF/6-31G* and UMP2/6-31G*, are yielding rather unusual results for BO_2 . Previous theoretical investigations were apparently restricted to $D_{\infty h}$ symmetry.^{29,30,31}

The energy differences (see Table 1) between the constrained $D_{\infty h}$ and $C_{\infty v}$ forms of BO_2 should be noted. At the highest level of theory at which geometry optimizations were carried out, MP2/6-31+G*, $C_{\infty v}$ OBO is 23 kJ mol⁻¹ lower in energy than the $D_{\infty h}$ structure. Consideration of zero point energy corrections reduces this energy difference due to the large imaginary vibrational frequency of the $D_{\infty h}$ form. The $D_{\infty h}$ isomer has ~ 13 kJ mol⁻¹ less zero point vibrational energy than the $C_{\infty v}$ species using the MP2/6-31+G* vibrational frequencies from Table 1. Higher level single point energy calculations, PMP4/6-31+G*, at the UMP2 geometries place the $D_{\infty h}$ BO_2 structure 9.7 kJ mol⁻¹ lower than the $C_{\infty v}$. Electron correlation effects at the UMP2 level for structure and the PMP4 level for relative energies begin to favor the experimentally observed $D_{\infty h}$ species in comparison to the unusual $C_{\infty v}$ prediction which is probably an artefact of the single configuration starting point.

The $^2\Sigma^+$ electronic state of BOO was found to be a minimum energy structure with a BO distance of 1.364 Å and an OO distance of 1.211 Å at the UMP2/6-31+G* level. The BOO structures are very different at the UHF and UMP2 levels in terms of the BO lengths. The correlated level results are probably more reliable. For example, at the UHF level relaxing the linear angle by one degree produced a *decrease* in energy, but this abnormality did not occur at the UMP2 level. The MP2/6-31+G* predictions of the vibrational frequencies after scaling by 0.95 are σ 1879 cm⁻¹, σ 732 cm⁻¹, and π 306 cm⁻¹.

Table 1

Energy (a.u.), geometry (Å) and frequencies (cm⁻¹) of BO₂ minima

Level of theory	Energy	Scaled vibrational frequencies		
$C_{\infty v} \quad ^2\Sigma^+ \quad \text{BOO}$				
UHF/6-31G*	-174.18856	σ 1902	σ 180	π 96
UMP2/6-31G*	-174.59101	σ 1881	σ 734	π 322
UHF/6-31+G*	-174.19624	σ 1898	σ 185	π 97
UMP2/6-31+G*	-174.60784	σ 1879	σ 732	π 306
PMP4/6-31+G*(a)	-174.63176	$\langle S^2 \rangle = 0.84$		
$C_{\infty v} \quad \text{OBO}$				
UHF/6-31G*	-174.43582	σ 1864	σ 932	π (419,469)
UMP2/6-31G*	-174.83387	σ 2141	σ 920	π (428,458)
UHF/6-31+G*	-174.44196	σ 1876	σ 930	π (424,478)
UMP2/6-31+G*	-174.84615	σ 2480	σ 911	π (434,475)
PMP4/6-31+G*(a)	-174.86790	$\langle S^2 \rangle = 0.79$		
$D_{\infty h} \quad \text{OBO}$				
UHF/6-31G*	-174.43582	σ 1017	π (341,458)	σ 2116i
UMP2/6-31G*	-174.82535	σ 1090	π (477,481)	σ 4269i
UHF/6-31+G*	-174.43654	σ 1012	π (343,466)	σ 2380i
UMP2/6-31+G*	-174.83741	σ 1080	π (488,494)	σ 4851i
PMP4/6-31+G*(a)	-174.87158	$\langle S^2 \rangle = 0.94$		

(a) at the UMP2/6-31+G* geometry

They verify that this species is a minimum with a reasonably large bending frequency. This BOO isomer lies *ca.* 600 kJ mol⁻¹ above $D_{\infty h}$ OBO at the MP2/6-31+G* level. Preliminary studies of several ($^2A_1$, $^2A_2$) bent electronically excited state minima of BO₂ were made at the UHF level but the wavefunctions showed internal instabilities. Such structures are being reexamined by us with more flexible theoretical approaches.

Figure 2 shows UHF/6-31G* optimized geometries for a number of AlO₂ species. The total energies are collected in Table 2. All these species are minima at the UHF/6-31G* level as verified by vibrational analysis with $D_{\infty h}$ OAIO the lowest energy molecule. Single point UMP4 energies at these UHF optimized structures indicate all these species are relatively low in energy, i.e. within ~ 120 kJ mol⁻¹ of the $D_{\infty h}$ OAIO minimum.

The results of two matrix isolation experiments^{32,33} on the reaction of Al with O₂ in frozen N₂ or Ar matrices have been reported. Both a C_{2v} AlO₂ geometry³² and a C_s

Figure 2. Geometries optimized at the UHF/6-31+G* theoretical level for six AlO_2 stationary points.

Table 2

Total energies (in a.u.) for UHF optimized minimum energy structures of AlO_2 . UHF and UMP4 energies with the 6-31+G* basis are reported along with $\langle S^2 \rangle$. The scaled UHF vibrational frequencies also are summarized (cm^{-1}). (See also Fig. 2)

State	UHF	$\langle S^2 \rangle$	UMP4	Scaled UHF Vibrational Frequencies			
$^2\text{A}'$	-391.53117	0.77	-391.94133	a' 1161	a' 564	a' 124	
$^4\text{B}_2$	.59642	3.77	.94175	b_2 754	a_1 674	a_1 217	
$^2\text{A}_1$	.51431	0.75	.95440	a_1 942	b_2 681	a_1 674	
$^2\Sigma_u$	.54366	1.17	.95492	σ_u 890	σ_g 623	π_u 160	
$^2\text{A}_2$	.53982	0.78	.96934	a_1 1277	a_1 495	b_2 89	
$^2\Pi_g$	.57000	1.16	.98538	σ_u 1764	σ_g 695	π_u (380,203)	

AlOO structure³³ have been suggested on the basis of the observed infrared spectra. More recent matrix isolation studies by Serebrennikov and coworkers have given evidence for a linear triatomic OAlO molecule.^{34,35} Two computational studies^{11,36} have found a $^2\text{A}_2$ C_{2v} minimum but no AlOO species was located. Only one of these studies³⁶ considered $\text{D}_{\infty h}$ OAlO while the other¹¹ emphasized the difficulty in describing the AlO_2 species due to a Hartree-Fock instability problem.

Our UHF/6-31+G* calculations indicate that there is a lowlying $^2\text{A}_2$ AlO_2 molecule with a cyclic superoxide geometry. The OO distance is predicted to be 1.298 Å with the experimental distance in the superoxide ion being *ca.* 1.26 Å. The Al is 1.932 Å from either oxygen thus resulting in a very sharp OAlO angle of 39.3°. The scaled vibrational

frequencies are $\nu_1(a_1)$ 1277 cm^{-1} , $\nu_2(a_1)$ 495 cm^{-1} , and $\nu_3(b_2)$ 89 cm^{-1} and are in moderate agreement with the values assigned earlier by Serebrennikov *et al.*³² The $^2A'$ AlOO species which was located at a UHF level has a predicted O-O stretch of 1161 cm^{-1} which is 176 cm^{-1} below the assignment of Sonchik *et al.*³³ However, initial attempts to locate this AlOO species at the UMP2/6-31+G* failed and its existence is somewhat uncertain. Note that $\langle S^2 \rangle$ is in the range 0.75 to 0.78 for the C_{2v} or C_s doublet species and thus spin contamination is not serious.

The UHF wavefunctions for all the lower symmetry bent species are stable while the $^2\Sigma_u$ and $^2\Pi_g$ linear OAIO molecular wavefunctions each show an instability.⁹ The consequences of this Hartree-Fock instability were explored for the lower energy, formally $^2\Pi_g$, OAIO species. The ordinary UHF/6-31+G* procedure predicted a bond length of 1.655 Å and all the calculated vibrational frequencies were real. However, the UHF wavefunction was checked and found to have an internal instability. At the geometry pictured in Fig. 2, the UHF result was reoptimized to a stable wavefunction and the $\langle S^2 \rangle$ decreased from 1.16 to 0.76 and the total energy decreased from -391.57001 a.u. to -391.57909 a.u. Using the reoptimized UHF wavefunction and a pointwise geometry search, a $C_{\infty v}$ OAIO molecule with two different bond lengths of 1.726 Å and 1.577 Å was located. This $C_{\infty v}$ OAIO species is 44 kJ mol^{-1} lower than the $D_{\infty h}$ geometry with ordinary UHF or 20 kJ mol^{-1} with the higher symmetry species described by a stable UHF wavefunction. Thus the $D_{\infty h}$ OAIO differs from $D_{\infty h}$ OBO in appearing to be a minimum according to its predicted vibrational frequencies. However, symmetry breaking distortions from $D_{\infty h}$ to $C_{\infty v}$ at least at the UHF level again are favored energetically. A modest multiconfiguration wavefunction will provide a much more adequate starting point for describing the electronic structure of $D_{\infty h}$ AlO₂.

It should be noted that many of our UHF results are in close agreement with an unpublished report by Arnau *et al.*³⁶ However, these workers did not investigate the effects of electron correlation nor consider the Hartree-Fock instabilities or symmetry breaking problems.

3.3 The Geometries and Vibrational Frequencies of BCO₂ and AlCO₂

The UHF/6-31G* predictions for the geometries of a C_{2v} *box* and C_s *cis*- and *trans*-isomers of BCO₂ are shown in Fig. 3. The scaled vibrational frequencies for these molecules along with BO, CO, and CO₂ are collected in Table 3. As will be discussed later, these three BCO₂ minima lie very close in energy.

For structural comparisons the (U)HF/6-31G* predicted bond lengths for BO, CO, and CO₂ should be noted to be 1.187, 1.114, and 1.143 Å respectively. There is some spin contamination for *cis*- and *trans*-BCO₂ with $\langle S^2 \rangle$ of 0.89 and 0.87. In the *cis* and *trans* complexes of BCO₂ the CO bond not attacked by the B atom lengthens only slightly, by 0.012 to 0.014 Å, relative to its value in CO₂. Naturally the other CO distance increases markedly to 1.349 Å in *trans*-BCO₂ or 1.346 Å in *cis*-BCO₂. At the HF/6-31G* level, a CO double bond in formaldehyde has a length of 1.184 Å while a CO single bond length in methanol is 1.400 Å. Thus there remains some multiple bond character in the stretched CO bond. The BO distances in these two complexes of 1.324 and 1.333 Å are ~0.06 Å greater than the experimental bond length in BO₂. The OCO and BOC bond angles are all within 2.5° of 130°. The strongly bent CO₂ fragment is somewhat suggestive of a B⁺(OCO)⁻ structure given that the bond angle in CO₂⁻ is about 135°. ³⁷

Figure 3. Optimized structures at the UHF/6-31G* level for box, *cis*, and *trans* BCO₂.

Table 3
HF/6-31G* frequencies at stationary points in B + CO₂ PES, scaled by 0.9 (cm⁻¹)

	BO	CO	CO ₂	<i>trans</i> -BOCO	<i>cis</i> -BOCO	<i>box</i> -BO ₂ C
ν_6	1886	2198	671	114	47	400
ν_5			671	209	188	665
ν_4			1355	585	647	904
ν_3			2321	970	971	1113
ν_2				1257	1213	1173
ν_1				1921	1894	1229
	TS1	TS2	TS3	TS4	TS5	OBCO
ν_6	532i	1384i	103i	627i	581i	201
ν_5	173	275	219	92	179	308
ν_4	546	476	613	196	581	516
ν_3	578	759	950	367	705	653
ν_2	1208	1141	1263	1215	1453	1926
ν_1	2106	1363	1907	2089	1616	2010

The C_{2v} BO₂C box has an interesting structure with the B 1.384 Å and the C 1.356 Å from the oxygens. The OBO and OCO bond angles are, of course, very small at 93.9° and 96.5°, respectively. This molecule illustrates that the B atom must interact strongly

with both O atoms to overcome the strain in the OCO moiety. The somewhat tortured nature of the electronic distribution in this *box* isomer is reflected in the existence of a UHF instability. Spin contamination is small for the conventional UHF wavefunction of the *box* isomer with an $\langle S^2 \rangle$ of 0.75. Very recently Andrews proposed an OBCO adduct.³⁸ UHF/6-31G* calculations place this isomer *ca.* 200 kJ mol⁻¹ lower in energy than *trans*-BOCO. Correlation effects at the UMP4/6-31G* level increase this difference to *ca.* 240 kJ mol⁻¹. Frequencies are listed in Table 3 and further studies are in progress to find transition states linking the OBCO adduct to B + CO₂ or to other species examined to date.

The UHF/6-31G* scaled vibrational frequencies for the BCO₂ species in Table 3 serve as reasonable predictions for experimentalists seeking to trap these complexes. However, *vide infra*, strongly exothermic reactions to BO + CO would ensure a difficult experiment. *Cis*- and *trans*-BOCO could be readily distinguished from the *box* form by the stretch of the uncoordinated CO at ~ 1900 cm⁻¹. This frequency is also ~ 400 cm⁻¹ less than that in free CO₂, one of the probable starting materials in any attempted synthesis of the boron complexes.

The geometrical structures of the transition states located which connect various BCO₂ minima will be discussed briefly here (See Fig. 4). All the planar transition states have electronic wavefunctions of ²A' symmetry. The energetics are left to Sec. 4.4. The highly asymmetric structure of TS1 connects B + CO₂ with the BCO₂ complexes and from inspection of the transition vector probably leads to the *trans* species. The B atom is 2.0068 Å from the O in CO₂ which it is attacking and forms an angle of 71.6° to the carbon. The B is also quite close to the C. The CO₂ fragment bends away from the incoming boron with the OCO angle becoming 157.9. Even the CO bond towards which the boron is moving only lengthens very modestly to 1.190 Å. The transition state is planar at the UHF/6-31G* level as verified by vibrational frequency analysis.

TS2 and TS3 connect the *cis* isomer to the *box* and the *cis* to the *trans* conformations, respectively. In TS2, the BOC and OCO angles of 95.0° and 109.5° are intermediate between their values in the *cis* and *box* minima. A similar comment applies to the BO distance and the shorter of the CO bonds. The structure is again a planar one as confirmed by the vibrational frequencies. TS3 is a nonplanar internal rotation transition state connecting the *cis* and *trans* isomers. This internal rotation is a very facile motion as would be anticipated from the very low vibrational frequencies for twisting of 47 and 114 cm⁻¹ in *cis*- and *trans*-BOCO.

TS4 and TS5 are the critical transition state structures which connect the BCO₂ complexes formed from B + CO₂ via TS1 with the BO and CO products. TS4 arises from the *trans*-BOCO with the lengthening of the central CO bond from 1.349 to 1.745 Å. The BOC and OCO angles decrease to 114.3° and 123.2° and the BO length and particularly the other CO distance shrink towards their values in the free diatomic molecules. TS5 with the BOC angle of 79.0° and the OCO angle of 92.5° connects the *box* BCO₂ with BO and CO. The central CO distance is again large at 1.788 Å. Now the BO bond is more strongly shortened than in TS4 but the CO has an essentially double bond length of 1.208 Å. It would be intriguing to see if gas phase dynamics experiments could infer whether TS4 or TS5 was most important. Different vibrational and rotational energy distributions in the diatomic products are suggested by the rather distinct structural features of these two transition states.

Figure 4. Optimized geometries at the UHF/6-31G* level for transition states on the BCO_2 potential energy surface. TS1 connects $\text{B} + \text{CO}_2$ to *trans*-BOCO. TS2 connects *cis*-BOCO to *box*- BCO_2 . TS3 connects *cis*-BOCO to *trans*-BOCO. TS4 connects *trans*-BOCO to $\text{BO} + \text{CO}$. TS5 connects *box*- BCO_2 to $\text{BO} + \text{CO}$.

The structures and vibrational frequencies of the AlCO_2 minima are of special interest due to the very recent report³⁹ of a matrix isolation spectroscopic study of AlCO_2 complexes in solid argon. Consequently, minimum energy forms of AlCO_2 were optimized not only at the UHF/6-31G* level but also at UMP2/6-31G*. These geometries are shown in Fig. 5. Predictions of the vibrational frequencies to verify the minimum energy nature were made at *both* the SCF and Moller-Plesset levels and are given in Table 4.

Two more qualitative features of the structures in Fig. 5 and on the geometry changes with the inclusion of electron correlation should be noted. Starting from the UHF/6-31G* geometry of *cis*- AlOCO , a UMP2/6-31G* optimization was attempted but it resulted in a very near C_{2v} *box* minimum. This observation suggests but does not prove that at higher levels of theory the *cis*- AlOCO complex may not exist but rather collapse to the C_{2v} *box* AlCO_2 . At the UMP2 level, there is a very great change in the location of the

Figure 5. Optimized geometries at the UHF/6-31G* and UMP2/6-31G* theoretical levels for several isomers of AlCO_2 .

Table 4

Experimental³⁹ and theoretical vibrational frequencies (cm^{-1}) for two isomers of AlCO_2 . The scale factors for the UHF & UMP2 6-31G* computed frequencies were 0.90 & 0.95

Box	Exp.	UHF	UMP2	Trans	Exp	UHF	UMP2
ν_5 b_2	1444	1544	1517	ν_1 a'	1780	1857	1827
ν_1 a_1	1266	1382	1287	ν_2 a'	1147	1211	1081
ν_2 a_1	797	816	766	ν_3 a'	773	764	693
ν_3 a_1	428	378	390	ν_4 a'	469	457	421
ν_4 b_1	-	312	533	ν_6 a''	-	59	293
ν_6 b_2	214	117	200	ν_5 a'	-	44	141

aluminum in *trans*-AlOCO. With electron correlation, the Al is 1.894 Å from the oxygen while at the UHF level this distance was only 1.740 Å. Qualitatively most noticeable is the change in the AlOC angle from 157.6° (SCF) to 85.3° (UMP2). The geometry changes were so substantial that the correlated level structure is labelled "new *trans*" in the figure. Rather similar changes in the geometries of LiCO₂ and NaCO₂ upon inclusion of electron correlation have been reported recently.³⁷

The experimental vibrational spectra of AlCO₂ complexes in solid argon were interpreted³⁹ in terms of two geometrical isomers. The low temperature form had C_s symmetry with a large inequivalence in the two CO bonds. The higher temperature form had a ring structure in which the aluminum interacted symmetrically with the two oxygen atoms. The enthalpy difference between the two isomers was on the order of 1 kJ mol⁻¹. The UMP2/6-31G* structures in Fig. 5 and vibrational frequencies in Table 4 generally support the experimentalists' interpretations. There are both the C_s *trans* and C_{2v} *box* minima which at present levels of theory lie within 10 kJ mol⁻¹ of one another. In the *trans* isomer, the two CO bond lengths of 1.311 and 1.198 Å are strongly inequivalent. The numerical values of the UMP2 vibrational frequencies in Table 4 show good agreement with the experimental assignments. The absolute average deviation of theory from experiment for these vibrational frequencies is only 35 cm⁻¹ for the C_{2v} and 60 cm⁻¹ for the C_s isomer. These deviations are only very slightly larger than typical for the theoretical model used.

The UHF/6-31G* transition state structures for the AlCO₂ potential energy surface are shown in Fig. 6, and their frequencies are listed in Table 5. The electronic wavefunctions are of ²A' symmetry. In comparison with Fig. 4, the most remarkable features of these transition state geometries are the general similarities between the BCO₂ and AlCO₂ structural results despite the rather different reaction energies (*vide infra*). TS1 connecting Al + CO₂ to *trans*-AlOCO is clearly reminiscent of the addition transition state for B + CO₂. In particular, the CO₂ fragment bends away from the incoming aluminum which approaches to 2.293 Å from the oxygen at an 87.6° angle to carbon. The Al is 2.538 Å from the C. TS2 and TS5 link *trans*-AlOCO and *box*-AlCO₂ to the diatomic molecules, AlO + CO. Very comparable qualitative structural results were presented in Fig. 4 for the fragmentations of the BCO₂ complexes. For AlCO₂, TS2 has a long CO distance of 1.766 Å and a relatively long AlO distance of 1.767 Å in comparison to the

Table 5
UHF/6-31G* frequencies for transition states on the Al + CO₂ PES, scaled by 0.9 (cm⁻¹)

	TS1	TS2	TS3	TS5
ν ₆	660i	585i	104i	636i
ν ₅	154	102	302	203
ν ₄	352	104	450	456
ν ₃	510	355	795	644
ν ₂	1146	673	1301	779
ν ₁	2133	2065	1649	1223

Figure 6. Structures optimized at the UHF/6-31G* level for transition states on the AlCO₂ potential energy surface. TS1 connects Al + CO₂ to *trans*-AlOCO. TS2 connects *trans*-AlOCO to AlO + CO. TS3 connects *cis*-AlOCO to *box*-AlCO₂. TS5 connects *box*-AlCO₂ to AlO + CO.

SCF result on free diatomic AlO of 1.697 Å. The CO distance of 1.124 Å is, on the other hand, only 0.01 Å longer than in carbon monoxide. The AlOC and OCO angles have decreased by ~49° and ~8° from their values in *trans*-AlOCO.

TS5 connects the C_{2v} *box* AlCO₂ to the product diatomic molecules and shows a shorter AlO bond than in TS2. The CO distance between the diatomic fragments is quite long at 1.907 Å and the AlOC and OCO angles of 76.4 and 99.6° are comparable to the values found for the boron species. The diatomic CO bond is rather long at 1.306 Å in this transition state. Rather different product internal energy differences could be inferred from the distinct geometries of TS2 and TS5.

In summary, our theoretical results to date have provided considerable insight into the reactions of B and Al atoms with small molecules and especially carbon dioxide. However, highly reliable quantitative data on the structures and energetics has not yet been

attained for all species. Intriguing computations remain particularly for molecules such as BO_2 which show Hartree-Fock instabilities and/or symmetry breaking.

4. THERMOCHEMICAL ANALYSIS

4.1 Thermochemistry of BO and AlO

Ab initio estimates of the dissociation energy D_e of BO, measured from the bottom of the potential well, have been determined in two ways. First, the energy change for $\text{BO} \rightarrow \text{B} + \text{O}$ was computed directly at several levels of theory. An alternative approach is to calculate the energy change for $\text{BO} \rightarrow \text{B}^+ + \text{O}^-$, and then to obtain D_e by taking into account experimental values of the ionization energy of B and the electron affinity of O.⁴⁰ This second approach might be expected to minimize errors arising from changes in the electron correlation energy for species with significant ionic character.⁴¹ The results of both methods are summarized in Table 6. The data for direct dissociation are almost independent of the size of the basis set employed but with the breaking of electron pairs depend strongly on the treatment of electron correlation. UMP4 theory is required to obtain D_e values to within about 30 kJ mol^{-1} of experimental values. For BO, analysis of D_e via dissociation to ions offers little advantage.

Table 6
Computed values of D_e for $\text{BO} \rightarrow \text{B} + \text{O}$ at different levels of theory (kJ mol^{-1})

Theory	Direct D_e	D_e via ions
UHF/6-31G*	560	828
UMP2/6-31G*	840	997
UMP4/6-31G*(a)	789	953
UHF/6-31+G*	557	716
UMP2/6-31+G*	847	848
PMP4/6-31+G*	780	789
UHF/6-311+G*	553	723
UMP2/6-311+G*	826	856
Expt. (Ref. 40)	810 ± 20	

A similar analysis was carried out for AlO and yields, e.g., $D_e = 424 \text{ kJ mol}^{-1}$ at the PMP4/6-31+G*//UMP2/6-31+G* level, which is significantly smaller than the experimental value of 508 kJ mol^{-1} . However, the UHF instability discussed in Section 3.1 means that many-body perturbation theory cannot be applied as reliably. Application of QCISD(T) theory at the UHF/6-31G* geometry yields a marginally improved D_e of 437 kJ mol^{-1} . CASSCF calculations avoid the HF instability problem and should give better estimates of D_e but Das *et al.*⁴² found a D_e of only 409 kJ mol^{-1} while the another theoretical estimate of D_e is 473 kJ mol^{-1} by Lengsfeld and Liu.²³ Recently, the G2

method for theoretical thermochemistry⁴³ has been used to estimate $D_e(\text{AlO})$ and $D_e(\text{BO})$.⁴⁴ This method corrects for higher order basis set and electron correlation effects assuming the changes to be approximately additive and yields values of D_e for BO and AlO of ca. 815 and 502 kJ mol⁻¹ respectively. These values are in excellent agreement with experiment.

4.2 Thermochemistry of the Reaction of B with O₂

B atoms may react with O₂ to form ground-state products via one of three channels:

The D_e values for BO discussed in the previous section were corrected for ZPE using frequencies scaled as outlined in Section 2.1. Combination with *ab initio* data for O₂ leads to the theoretical values for ΔH°_0 for reaction (2a) summarized in Table 7. Typical changes in ZPE between reactants and products in these reactions are in the range 3 to 10 kJ mol⁻¹, so that a 10% error in predicted frequencies will lead to negligible errors in ΔH°_0 .

Table 7

Calculated ΔH°_0 for $\text{B} + \text{O}_2 \rightarrow \text{BO} + \text{O}$ (kJ mol⁻¹)

Theory	ΔH°_0	Theory	ΔH°_0
UHF/6-31G*	-458	MP4/6-31+G*(a)	-327
UMP2/6-31G*	-352	UHF/6-311+G*	-423
UMP4/6-31G*(a)	-326	UMP2/6-311+G*	-329
UHF/6-31+G*	-324	Expt. (ref. 40)	-311 ± 20
UMP2/6-31+G*	-252		

(a) At the UMP2/6-31+G* geometry.

Table 8

ΔH°_0 relative to $\text{B} + \text{O}_2$ (kJ mol⁻¹). UHF & UMP2 frequencies scaled by 0.9 & 0.95

Theory	$C_{\infty v}$ BOO	$C_{\infty v}$ OBO	$D_{\infty h}$ OBO
UHF/6-31G*	-132	-795	-793
UMP2/6-31G*	-208	-841	-831
UHF/6-31+G*	-18	-654	-652
UMP2/6-31+G*	-115	-737	-725
PMP4/6-31+G*(b)	-183	-798	-820

(b) At the UMP2/6-31+G* geometry.

of up to 1 kJ mol⁻¹. The UMP4 results agree with experiment within the quoted uncertainty.⁴⁰

The most exothermic channel is (2b), and the results of Table 8 show that reasonable accord with the experimental ΔH° is obtained provided corrections for electron correlation are included. At the highest level of theory ΔH° is predicted to be -820 kJ mol⁻¹ which is just within the error bar of the experimental value.⁴⁰ Thus theory and experiment are in quite satisfactory accord for these simple boron oxides. There are no experimental data for reaction (2c). Our best estimate is that ΔH° is *ca.* -183 kJ mol⁻¹, so that BOO is thermodynamically unstable with respect to dissociation to BO + O and to isomerization to OBO.

4.3 Thermochemistry of the Reaction of Al with O₂

Analogous channels for the reaction of Al with O₂ are

Reaction (3a) cannot be analyzed rigorously because of the problem with the instability of the wavefunction for AlO. The most stable AlO₂ isomer, ²Π_g OAlO, lies 273 kJ mol⁻¹ below Al + O₂ at the UMP4/6-31+G*//UHF/6-31+G* level (including ZPE). However, this wavefunction is UHF unstable. Repeating this calculation with a reoptimized and stable wavefunction yields $\Delta H^\circ = -295$ kJ mol⁻¹. Allowance for spin-contamination effects probably will reduce ΔH° for reaction (3b) by *ca.* 50 kJ mol⁻¹, but this theoretical value still would fall short of the experimental estimate of -412 ± 36 kJ mol⁻¹.⁴⁰ Very recent G2 calculations on OAlO are in accord with the experimental thermochemistry,⁴⁴ despite the presence of HF instability. No reliable energy is yet available for AlOO to establish the probable stability of this isomer. Further theoretical work is required to understand the thermochemistry of these aluminum oxides.

4.4 Thermochemistry of the Reaction of B with CO₂

Our best *ab initio* estimate of ΔH° for the overall reaction to BO + CO is -259 kJ mol⁻¹ (see Table 9). This lies just within the experimental range -279 ± 20 kJ mol⁻¹.⁴⁰ Two new adducts between B and CO₂ have been proposed here. *Trans*-BOCO is estimated to lie 106 kJ mol⁻¹ below B + CO₂ at the PMP4/6-31G*//UHF/6-31G* level (including ZPE). *cis*-BOCO is 9 kJ mol⁻¹ less stable than this *trans* species. No experimental data exist for the adducts but a reasonable estimate of the uncertainty in these ΔH° values, based on the comparison for BO + CO, is *ca.* ± 20 kJ mol⁻¹. The transition state between the two isomers (Fig. 4) found at the UHF/6-31G* level in fact has an intermediate energy at the PMP4 level, thus isomerization may be regarded as a hindered internal rotation. The C_{2v} BO₂C adduct (Fig. 3) is estimated to be bound by ~ 96 kJ mol⁻¹ relative to B + CO₂. This value was obtained using a HF unstable wavefunction and further optimization may increase slightly this B-CO₂ bond strength.

4.5 Thermochemistry of the Reaction of Al with CO₂

PMP4 theory (Table 10) suggests that *trans* AlOCO is bound by ~ 43 kJ mol⁻¹ relative to Al + CO₂ at 0 K. The *cis* isomer is only 1 kJ mol⁻¹ less stable than the *trans*.

Table 9

Calculated energies of stationary points on the B + CO₂ potential energy surface (a)

species	HF energy, au	MP4 energy, au (b)	PMP4 energy, au (b)	<S ² >	ZPE, au	MP4 H ₀ , kJ mol ⁻¹ (c)	PMP4 H ₀ , kJ mol ⁻¹ (c)
B	-24.52204	-24.57594	-24.57623	0.75	0	0	0
CO ₂	-187.63418	-188.12442	-188.12442	0	0.01143		
BO	-99.51995	-99.76733	-99.76993	0.80	0.00430		
CO	-112.73788	-113.02731	-113.02731	0	0.00501	-253	-259
<i>trans</i> BOCO	-212.19017	-212.73580	-212.74115	0.89	0.01152	-93	-106
<i>cis</i> BOCO	-212.18706	-212.73286	-212.73752	0.87	0.01130	-86	-97
<i>box</i> BO ₂ C	-212.19322 ^d	-212.73788	-212.73816	0.75	0.01250	-96	-96
TS1	-212.12563	-212.69055	-212.69389	0.82	0.01051	+23	+15
TS2	-212.18640	-212.73321	-212.73810	0.87	0.01128	-38	-51
TS3	-212.18640	-212.73321	-212.73810	0.87	0.01128	-87	-99
TS4	-212.16748	-212.71836	-212.73009	1.03	0.00902	-54	-84
TS5	-212.16998	-212.73011	-212.73096	0.76	0.01033	-81	-82

(a) Data obtained at the optimized UHF/6-31G* geometries with UHF/6-31G* frequencies scaled by 0.9.

(b) Frozen core MP4 and spin-projected PMP4 calculations at the UHF/6-31G* geometries.

(c) Enthalpies relative to B + CO₂ at 0 K.(d) *box* BO₂C is HF unstable.

Table 10

Calculated energies of stationary points on the Al + CO₂ potential energy surface (a)

species	HF energy, au	MP4 energy, au (b)	PMP4 energy, au (b)	<S ² >	ZPE, au	MP4 H ₀ , kJ mol ⁻¹ (c)	PMP4 H ₀ , kJ mol ⁻¹ (c)
Al	-241.85698	-241.89950	-241.89986	0.76	0	0	0
CO ₂	-187.63418	-188.12442	-188.12442	0	0.01143	0	0
<i>trans</i> AlOCO	-429.50316	-430.03755	-430.03915	0.77	0.01001	-40	-43
<i>cis</i> AlOCO	-429.50390	-430.03751	-430.03903	0.77	0.01028	-39	-42
<i>box</i> AlO ₂ C	-429.50093	-430.04218	-430.04350	0.76	0.01036	-51	-53
TS1	-429.46785	-430.01840	-430.02013	0.79	0.00978	+10	+6
TS2	-429.46145	-429.99696	-430.00284	0.84	0.00751	+60	+46
TS3	-429.50037	-430.04008	-430.04146	0.77	0.01024	-46	-48
TS5	-429.36232	-429.86415	-429.87596	1.81	0.00753	+409	+379

(a) Data obtained at the optimized UHF/6-31G* geometries with UHF/6-31G* frequencies scaled by 0.9.

(b) Frozen core MP4 and spin-projected PMP4 calculations at the UHF/6-31G* geometries.

(c) Enthalpies relative to Al + CO₂ at 0 K.

No barrier is found to essentially free internal rotation about the O-C bond. There is also no barrier at the PMP4 level to isomerization of *trans*-AlOCO to C_{2v} AlO₂C, which is predicted to lie ~ 53 kJ mol⁻¹ below Al + CO₂.

These results are in qualitative accord with the lower limit to the Al-CO₂ bond energy of >38 kJ mol⁻¹ assigned by Parnis *et al.*,⁴⁵ and also the recent matrix-isolation experiments by Le Quéré *et al.*³⁹ Le Quéré *et al.* showed, based on the observation of reversible isomerization between *trans/cis* and C_{2v} forms at about 20 K, that there is a minimal barrier to interconversion, in accord with theory. In that work ΔH° for *trans* $\rightarrow$ C_{2v} was determined to be $+1.55 \pm 0.4$ kJ mol⁻¹ in the frozen matrix, rather than the *ca.* -10 kJ mol⁻¹ predicted here for the gas phase. It is possible that interactions with the matrix contribute to this difference between experiment and theory.

We have also calculated equilibrium constants for $Al + CO_2 \rightleftharpoons C_{2v} AlO_2C$ by statistical mechanics to yield $K_{eq} \approx 3.4 \times 10^{-24} \exp(-6140/T) \text{ cm}^3$ for the *ab initio* Al-CO₂ bond energy of 53 kJ mol⁻¹. As the temperature increases the stability of the adduct will decrease. The K_{eq} expression implies that in typical kinetic experiments, where $[CO_2] \approx 10^{17} \text{ cm}^{-3}$, adduct formation will become negligible above *ca.* 450 K. Garland¹ was able to measure adduct formation at up to 600 K, which suggests that a better estimate of the Al-CO₂ bond energy may be about 70 kJ mol⁻¹. Thus an estimated uncertainty of ± 20 kJ mol⁻¹ appears reasonable for the theoretical ΔH°_0 values in the Al + CO₂ system.

5. KINETIC ANALYSIS

5.1 Kinetics of the Reaction of B with O₂

Consideration of adiabatic state symmetry rules⁴⁶ for $B + O_2$ and $BO + O$ shows that the six surfaces arising from $B \ ^2P^\circ + O_2 \ X \ ^3\Sigma_g^-$ correlate with all the surfaces originating from $BO \ X \ ^2\Sigma^+ + O \ ^3P$. Thus $BO \ A \ ^2\Pi$, while accessible energetically,²⁰ can only be formed in a non-adiabatic process. This non-adiabaticity is consistent with the observation that most $A \rightarrow X$ chemiluminescence observed in the reaction of $B + O_2$, even at low pressures, arises from efficient collision-induced $V \rightarrow E$ energy transfer within highly vibrationally excited $BO \ X \ ^2\Sigma^+$.⁴⁷

We have studied the lowest energy potential energy surface connecting $B + O_2$ with $BO \ X \ ^2\Sigma^+ + O \ ^3P$ and with $OBO \ X \ ^2\Pi$ by *ab initio* methods. Preliminary scans indicated that the minimum energy pathway for reaction is sideways attack on O₂ to form OBO. A possible interpretation is that the B atom partially bonds to both O atoms during sideways attack, rather than just one O atom during end-on attack (*cf.* Section 3.3). This idea is consistent with the much greater stability of OBO with respect to BOO (Section 4.2). Part of the energy surface, where C_{2v} symmetry is maintained during insertion of B into O₂, was investigated at the UMP2/6-31G* level and is shown in Fig. 7. The distance from B to the center of O₂ was varied, while allowing the O-O distance to relax to its optimal value. The reaction proceeds initially along a $^2A_2$ surface, followed by allowed transitions to a $^2A_1$ and then a $^2B_2$ surface, with no significant energy barriers between reactants and products. In principle, it might be possible to isolate bent $^2A_1$ BO₂ in a frozen matrix, but in the gas phase conversion to linear OBO will be rapid. Figure 8 summarizes UMP2/6-31G* data for the dissociation of OBO to $BO + O$ while maintaining $C_{\infty v}$ symmetry. There is no barrier to this process beyond the endothermicity.

Figure 7. Part of the PES for $B + O_2 \rightarrow OBO$, with C_{2v} symmetry maintained, at the MP2/6-31G* level.

Figure 8. Part of the PES for $OBO \rightarrow BO + O$, with $C_{\infty v}$ symmetry maintained, at the MP2/6-31G* level.

Another possible reaction channel involves end-on addition of B to O_2 in $C_{\infty v}$ symmetry to form linear BOO. At the UMP2/3-21G level no barrier to this addition was found, and this species may be observable by matrix isolation techniques. However, a potential curve which corresponds to dissociation to $BO + O$ intersects the curve for BOO

close to its minimum and provides a pathway for initially excited BOO to decompose easily in the gas phase. Thus both end-on and sideways attack by B on O₂ can lead to BO formation with no energy barrier; the relative importance of each channel is an interesting problem for a dynamical trajectory study.

The kinetics of reaction (2) were analyzed by the QRRK method as outlined in Section 2.2. This analysis does not distinguish between sideways and end-on trajectories. The enthalpies of OBO and BO + O relative to B + O₂ discussed in Section 4.2, of -820 and -327 kJ mol⁻¹, respectively, were employed together with an *ab initio* geometric mean vibrational frequency for OBO of $\bar{\nu} = 740$ cm⁻¹. Lennard-Jones parameters for OBO, necessary for estimation of the collision rate with the Ar bath gas, were assumed to be $\sigma = 3.0$ Å and $\epsilon/k_B = 1000$ K. The results are only weakly sensitive to the exact values employed. Polarizability data⁴⁸ for B and O₂ yield a rate constant for surmounting the centrifugal barrier and forming OBO* of $k_f = 7.0 \times 10^{-11} T^{1/6} \text{ cm}^3 \text{ s}^{-1}$ (all concentrations are in molecule cm⁻³). Because OBO* is formed with an internal energy some 300 kJ mol⁻¹ above the dissociation energy to BO + O, $k_p(E) \gg \beta k_s[\text{Ar}]$ even at a pressure of 100 atm and so stabilization of OBO may be ignored. Thus BO + O are predicted to be the only significant products, and the total rate constant for reaction (2), k_2 , will be pressure-independent with $k_2 = k_f$. k_2 is predicted to increase from $1.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 298 K to $2.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 2000 K. This theoretical estimate is in reasonable accord with experiment. It is roughly a factor of two larger than the measurements of Oldenberg and Baughcum,⁴⁹ and reproduces the very weak temperature dependence which they measured. An earlier measurement of k_2 at 298 K by DiGiuseppe and Davidovits⁵⁰ lies a factor of 4 below our value. Thus the present theory may be ignoring some nonreactive trajectories.

The potential energy surface may also be employed to predict the kinetics of

Formation of B + O₂ is too endothermic to be significant. Polarizability data to derive C_6 in $V(r) = -C_6/r^6$ for BO + O interactions are unavailable, so C_6 was obtained instead by fitting to the *ab initio* data of Fig. 8. The predicted adduct formation rate constant, $k_f = 6.3 \times 10^{-11} T^{1/6} \text{ cm}^3 \text{ s}^{-1}$, is very similar to that for B + O₂. k_f corresponds to the high pressure limit for reaction (4), $k_{4,\infty}$. At 298 K the rate constant for formation of OBO is in the low-pressure regime below 1 atm, and the third-order recombination rate constant is $k_{4,0} = 2.0 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$. The falloff pressure $P_{1/2}$, where $k_4 = k_{4,\infty}/2$, is about 40 atm. $P_{1/2}$ increases with temperature and, at 2000 K, k_4 is in the low-pressure regime even up to 100 atm. $k_{4,0}$ decreases with increasing temperature, primarily because collisional stabilization by the bath gas becomes less efficient, and is summarized by the expression $k_{4,0} = 6.4 \times 10^{-27} T^{-1.82} \text{ cm}^6 \text{ s}^{-1}$. At present there are no experimental results for comparison, although there is reasonable accord with the predictions of Yetter *et al.*,^{51,52} which are a factor of 2.3 smaller at room temperature and 1.2 smaller at 2000 K.

5.2 Kinetics of the Reaction of Al with O₂

As for B + O₂, a preliminary survey of the potential energy surface indicates that the most favorable reaction pathway is attack on O₂ from the side, again suggesting the importance of Al interaction with both O atoms. UHF/6-31+G* data for the PES in C_{2v} symmetry indicate that at long range the Al-O₂ interaction occurs on a ²A₂ surface, similar

to $B + O_2$, and that there is no evidence for a barrier to insertion to form $OAIO$. By analogy with reaction (2) we assume that initially formed $OAIO$ may dissociate to $AlO + O$ with no barrier beyond the endothermicity. Experimental data yields energies of $OAIO$ and $AlO + O$, relative to $Al + O_2$, of -412 and -13 kJ mol^{-1} , respectively. The resulting potential energy surface was analyzed in a similar manner to that for $B + O_2$.

Based on our *ab initio* results we employ a geometric mean frequency of $\bar{\nu} = 555$ cm^{-1} for $OAIO$. Lennard-Jones parameters for $OAIO$ were assumed to be $\sigma = 3.95$ $\text{\AA}$ and $\epsilon/k_B = 1000$ K. Polarizability data⁴⁸ for Al and O_2 yield $k_f = 6.5 \times 10^{-11}$ $\text{cm}^3 \text{s}^{-1} \text{T}^{1/6} \text{cm}^3 \text{s}^{-1}$. No polarizability data are available for AlO , and thus we assumed k_f for $AlO + O$ to be identical to that for $Al + O_2$, by analogy with the $B + O_2$ reaction. Pre-exponential factors for the dissociation of $OAIO$ to $Al + O_2$ and $AlO + O$ were estimated as described in Section 2.2. The latter process has an A factor about 5 times larger than the former, which combined with the lower energy barrier to dissociation to $AlO + O$ allows this pressure-independent fragmentation to dominate collisional stabilization of $OAIO^*$. At 298 K, the branching ratio to $OAIO$ as a fraction of total Al consumption is about 0.3 at 100 atm, while at 2000 K and 100 atm this ratio is only 0.005. The low-pressure recombination rate constant for the minor channel $Al + O_2 + Ar \rightarrow OAIO + Ar$ is predicted to be $2.5 \times 10^{-29} \text{T}^{-1.18} \text{cm}^6 \text{s}^{-1}$.

Thus under most laboratory and combustion conditions $OAIO$ formation is negligible, and the total Al removal rate constant for reaction (2) is $k_3 \approx k_f$ for $Al + O_2$. The measurements of k_3 by Garland¹ are about 0.7 of this theoretical prediction, and show no pressure dependence between 10 and 100 Torr, in accord with the present analysis. There is, however, disagreement with the smaller k_3 values measured by Fontijn *et al.*,⁵³ but the very recent redetermination of k_3 by Fontijn and co-workers is close to our estimate.⁵⁴ The $\text{T}^{1/6}$ dependence suggested here for k_3 is closer to the T^0 dependence measured both by Fontijn *et al.* and Garland than e.g. the $\text{T}^{1/2}$ behavior predicted by simple collision theory.

We also analyzed the reverse reaction $AlO + O$, for which no experimental data are available. Both formation of $OAIO$ and $Al + O_2$ are possible channels. The rate constant k_3 for $Al + O_2$ formation is estimated as $4.6 \times 10^{-11} \exp(-1650/T) \text{cm}^3 \text{s}^{-1}$, while the third-order recombination rate constant to form $OAIO$ is $4.0 \times 10^{-27} \text{T}^{-1.68} \text{cm}^6 \text{s}^{-1}$. At 298 K, $P_{1/2}$ for recombination is about 30 atm. At 1 atm, the branching ratio for $OAIO$ formation is about 0.04 and decreases linearly with decreasing pressure. At 2000 K the branching ratio is about 2×10^{-4} at 1 atm, and even at 100 atm is only 0.016. Thus addition followed by fragmentation is the dominant reaction channel under most conditions.

5.3 Kinetics of the Reaction of B with CO_2

Three product channels were considered

The potential energy surface shown in Fig. 9 was employed in a QRRK analysis which incorporated isomerization between the adducts as well as possible dissociation of each adduct to $BO + CO$. Pre-exponential factors for these processes were estimated by

Figure 9. The PMP4/6-31G* PES used for the kinetic analysis of the $B + CO_2$ reaction.

transition state theory. k_f (see equation (1)) for the initial addition of B to CO_2 by passage through TS1 (see Fig. 9) was estimated by TST to be $1.4 \times 10^{-14} T^{1.17} \exp(-1680/T) \text{ cm}^3 \text{ s}^{-1}$. In this case, k_f represents the overall rate constant for consumption of B, k_s , which will be pressure independent. An Arrhenius plot of the calculated k_s is given in Fig. 10, together with the only measurement of k_s , by DiGiuseppe and Davidovits at room temperature.⁵⁰ Agreement is good, to within a factor of two, and can be made exact by a very small reduction of the calculated barrier at TS1, of only 1.7 kJ mol^{-1} . This adjustment is considerably smaller than the uncertainty in both the experimental and *ab*

Figure 10. Arrhenius plot of the *ab initio* rate constant for $B + CO_2$. (•) Measurement⁵⁰.

Figure 11. Branching ratio for BOCO adducts as a function of temperature with $P_{Ar} = 1$ atm.

Figure 12. Branching ratio for BOCO adducts as a function of argon pressure at 298 K.

initio enthalpies discussed earlier. Our expression for k_5 is, however, different from those given by Yetter *et al.*,^{51,52} which imply a negative temperature dependence and pre-exponential factors more than 3 orders of magnitude below the gas kinetic collision rate.

The ratios k_{5b}/k_5 and k_{5c}/k_5 are shown in Figs. 11 and 12 as functions of temperature and pressure. These ratios are small because the adducts are formed with excess internal energy over that required for dissociation. Formation of BO_2C is about 100 times less likely than formation of BOCO because reaction via TS2 (see Fig. 9) must compete with dissociation to $BO + CO$. Both routes have similar A factors, around 10^{13} s^{-1} , but the energy barrier to dissociation is 33 kJ mol^{-1} lower than the barrier to isomerization.

5.4 Kinetics of the Reaction of Al with CO_2

As noted in Section 3.3 the potential energy surface for

shown in Fig. 13 is qualitatively similar to that for $B + CO_2$ but there are important energetic differences. *Trans*-AlOCO is formed via TS1 with a lower energy barrier than for the analogous B reaction. However, the barrier to dissociation is now larger than the barrier back to reactants, which inhibits channel (6a). Unlike reaction (5), there is a negligible barrier between the *trans* and C_{2v} adducts which we therefore consider to isomerize rapidly. Lastly, the barrier to dissociation of *box* AlO_2C is predicted to be very large, more than 400 kJ mol^{-1} , and so direct decomposition of this species to $AlO + CO$ may be neglected.

There are extensive experimental data on reaction (6) at 298 K and we have used this information to guide the kinetic analysis. In particular, the *ab initio* barrier height at TS2 of 89 kJ mol^{-1} relative to *trans* AlOCO was almost certainly too high due to difficulties

Figure 13. The PMP4/6-31G* PES used for the kinetic analysis of the $\text{Al} + \text{CO}_2$ reaction. The barrier at TS2 has been adjusted to model experiment.

in describing the AlO product to which TS2 leads. Consequently, we reduced this barrier by 32 kJ mol^{-1} to 57 kJ mol^{-1} to model experiment. The only other adjustment was a very minor one involving the reduction of the barrier at TS1 by 0.5 kJ mol^{-1} . The data from Table 4 were used to estimate the mean $\bar{\nu}$ of 356 and 537 cm^{-1} for AlOCO and AlO_2C , respectively. Lennard-Jones parameters for both adducts were assumed to be $\sigma = 3.95 \text{ \AA}$ and $\epsilon/k_B = 1000 \text{ K}$. *Ab initio* bond energies (Section 4.5) were used without further adjustment.

The QRRK approach was employed to analyze the potential energy surface using the kinetic scheme of equation (1), with the addition of a fast reversible isomerization step between the two adducts. The pre-exponential factor for k_b of AlOCO is relatively small, around $2 \times 10^{12} \text{ s}^{-1}$ at 298 K , which inhibits decomposition back to $\text{Al} + \text{CO}_2$. The total Al removal rate constant $k_6 = k_{6a} + k_{6b} + k_{6c}$ predicted at 298 K is plotted as a function of pressure in Fig. 14. k_6 is in excellent accord with the experimental measurements of Garland¹ also shown there, which themselves agree well with the results of Parnis *et al.*⁴⁵ Our theoretical analysis therefore confirms the qualitative Lindemann mechanism for reaction (6) first proposed by Parnis *et al.* This mechanism is analogous to the reaction scheme outlined in equation (1) *except that the energy-dependence of k_b and k_p is ignored*. However, this difference makes direct quantitative comparison with the individual parameters determined by Parnis *et al.* and by Garland difficult.

We have calculated the low-pressure limiting rate constant $k_{6b,0} + k_{6c,0}$ as a function of temperature. From 298 to about 360 K this rate constant increases slightly, from about 5.3×10^{-31} to $6.0 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$, which reflects the increasing ease of crossing the small barrier to addition, but at higher temperatures the rate constant decreases, to about $1.5 \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ at 1000 K , because of the decreasing efficiency of collisional stabilization of the adducts. Also, as noted in Section 4.5, the adducts are insufficiently stable to be a

Figure 14. Total rate constant for $\text{Al} + \text{CO}_2$ as a function of Ar pressure at 298 K. Measurements¹ shown as ($\bullet$).

major sink for Al above approximately 600 K. Thus the contribution of adduct stabilization to k_6 may be ignored in combustion applications. The data of Garland and Parnis *et al.* at 298 K are already in the falloff regime and thus do not determine $k_{6,0}$ precisely. Measurements at pressures of *ca.* 0.1 to 1 Torr would provide a further test of theory in the low-pressure limit.

Figure 15. Arrhenius plot of the total rate constant for $\text{Al} + \text{CO}_2$ at two Ar pressures. Data from Ref. 1: ($\bullet$); data from Ref. 55: ($\circ$).

Figure 15 shows the Arrhenius plots of k_a at two pressures, and demonstrates that the pressure dependence will become negligible above about 800 K, in accord with experiment.¹ Two sets of high-temperature measurements^{1,55} are also shown in Fig. 15. Comparison with the theoretical values suggests that the A factor for reaction via TS2 is too large by roughly a factor of two. Thus TS2 appears to be that part of the potential energy surface most poorly characterized by theory. As theory already overestimates Al consumption at $T > 800$ K there may be no need to invoke a separate O-atom abstraction channel¹ to account for the reaction of Al. Thus far no such channel has been identified by the *ab initio* studies.

6. CONCLUSIONS

To date, the results of both the *ab initio* quantum chemical studies and the quantum RRK kinetic analysis have been on the whole highly satisfactory. In particular, the predicted vibrational spectra of the two AlCO_2 isomers are in very good agreement with experiment. Thermochemical predictions based largely on high level *ab initio* theory are in good agreement with experiment for the BO and BO_2 species. The energetics of the BCO_2 and AlCO_2 potential energy surfaces required only modest adjustment to provide parameters for the QRRK model, which then yielded kinetic parameters in good accord with most previous experimental measurements. Specifically, the QRRK model provides a reliable extrapolation of room temperature experiments on $\text{B} + \text{CO}_2$ to combustion conditions, and was able to reproduce the falloff behavior of the $\text{Al} + \text{CO}_2$ reaction at low temperatures and the lack of pressure dependence at high temperatures. For the $\text{B} + \text{O}_2$ and $\text{Al} + \text{O}_2$ systems the branching ratios of addition versus abstraction have been calculated for both the forward and reverse reactions.

Quantum chemical computations are continuing in order to better represent the molecules BO_2 and especially AlO and linear AlO_2 . The use of multiconfiguration self-consistent-field theory should resolve a number of current difficulties due to Hartree-Fock instabilities and symmetry breakings. Comparative studies of the QRRK model with the more elaborate RRKM procedure for several of these B and Al atom-molecule reactions will be undertaken.

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