



What are the main gas-phase species formed by aluminum when added to a premixed flame?

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Abstract

When aluminum is present in the burned gas of a flame at typically 1500–2700 K and 1 bar, there is doubt as to which are the principal species it forms in the gas phase. Quantum chemical computations with G3B3LYP theory have been performed on the 16 species Al, AlH, AlO, AlOH, HAIO, AlO₂, Al₂O, Al₂O₂, H₂AlO, HAIOH, OAlOH, Al(OH)₂, Al₂O₃, H₂AlOH, HAl(OH)₂, and Al(OH)₃. These calculations indicate that in the gas phase at 1 bar aluminum is present mainly as Al(OH)₃, AlOH, OAlOH, and AlO over the temperature range 1500–2700 K. In the hottest (>2500 K) rich or lean flames, AlOH dominates, whereas at relatively low temperatures (~1500 K), Al(OH)₃ is the major species, irrespective of the flame's composition. Even in a very oxygen-rich flame, molecular Al₂O₃ is usually one of the least abundant species of Al in the gas phase; this fact probably accounts for the relatively modest production of solid nanoparticles of Al₂O₃ in oxygen-rich flames doped with Al.

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1. Introduction

Even though aluminum is a common constituent of propellants, pyrotechnics, etc., there is great uncertainty as to which species it forms in the gas phase of a flame. Jensen and Jones [1] concluded from a spectrophotometric study that when small amounts of aluminum are added to fuel-rich, premixed flames of H₂ + O₂ + N₂ at atmospheric pressure, the principal compound formed by the metal in the gas phase is Al(OH)₂. However, they also decided [1] that there are lesser amounts of AlO and free atoms of Al. This was corroborated by Newman and Page [2], who

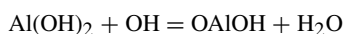
earlier had decided that HAIO was most probably the dominant species formed by Al in such a flame. A subsequent mass spectrometric study [3,4] of a lean flame of H₂ + O₂ containing Al indicated the presence of free atoms of Al, as well as AlO, AlO₂, AlOH, and OAlOH, with AlOH being the most abundant of these species. There was alleged [4] to be a somewhat smaller concentration of OAlOH; however, very little of the Al seemed to form Al(OH)₂. Subsequently, Goodings and co-workers [5] studied the very small concentrations of ions found in a fuel-rich flame of CH₄ + O₂ at 2200 K with ~1 ppm of Al present from nebulizing an aqueous solution of AlCl₃ into the gas supplied to the burner. Equilibrium calculations with thermodynamic data available at the time [6] indicated that in the gas phase, aluminum was present

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roughly as 73% OAlOH and 27% AlOH, all on a molar basis; at most ~0.1% of the Al was expected to exist as ions in the hotter flames. They accordingly expected the major species OAlOH to form the ion $\text{Al}(\text{OH})_2^+$ in a flame by proton transfer. Even though their mass spectrometer was sufficiently sensitive to detect ions with mole fractions as low as 10^{-15} , the ion $\text{Al}(\text{OH})_2^+$ was not observed, but its monohydrate $\text{Al}(\text{OH})_2^+ \cdot \text{H}_2\text{O}$ was. It is, of course, quite possible that any $\text{Al}(\text{OH})_2^+$ present was hydrated quickly during sampling, when the gas was cooled rapidly [7] on entering the mass spectrometer supersonically. Also, the observed ion $\text{Al}(\text{OH})_2^+ \cdot \text{H}_2\text{O}$ might be formed by proton transfer to $\text{Al}(\text{OH})_3$, another candidate as a major neutral species.

It can only be concluded from all this previous experimental work that there is considerable doubt as to which gas phase species are formed by aluminum when present in a flame. The situation is interestingly confused further by the current JANAF tables [8] not having any information on $\text{Al}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$; likewise, the NIST tabulations [9] do not have data on OAlOH and $\text{Al}(\text{OH})_3$. Gurvich et al. [10] list data for OAlOH and $\text{Al}(\text{OH})_3$, but their value for the heat of formation of OAlOH is quite different from that quoted in the JANAF [8] tables (−461 versus −356 kJ/mol). Of course, it is most likely that the concentrations of these two species (as with other pairs of species) are related, because gas phase equilibria such as



will be established quickly [1] in one of these flames.

During the past 20 years, great progress has been achieved in ab initio computational techniques. The newly developed computational methods, such as G3B3LYP, can be used to predict heats of formation for compounds in the first and second rows of the periodic table to an accuracy of ± 4.1 kJ mol^{−1} [11,12]. Recently, three papers [13–15] have applied high-level methods of quantum chemistry to compute the thermodynamic properties of various species formed by aluminum at high temperatures. However, none of these studies [13–15] covered all the above 16 important species; also, some reported values seem to have errors in the calculations, as discussed below. This work takes these computations farther. Here we report a complete set of computed thermochemical data using G3B3LYP theory over the usual range of flame temperatures of 1500–2500 K for all the neutral aluminum compounds (of the elements Al, O, and H) expected to exist in flames of $\text{H}_2 + \text{O}_2 + \text{N}_2$ doped with Al. Some species, such as Al_2O and AlH_2 , have been ignored, because they are not expected to be important in the flames considered below.

2. Computational methods

The Gaussian 03 package [16], together with the very accurate G3//B3LYP method [12], was used for the computations. G3//B3LYP theory is a modification of G3 theory, in which the geometries and zero-point energies are obtained from B3LYP density functional theory, while the calculation of energy is similar to G3 theory, in that it combines a series of smaller computations to approximate the calculation of a quadratic configurational interaction [11,12]. Computations using G3//B3LYP theory provide the equilibrium geometric structure and also the vibrational frequencies, internal energies, entropies, and Gibbs free energies at a given temperature for a molecule [11–15]. The standard enthalpies of formation can then be calculated from the computed enthalpies of atomization and the well-established enthalpies of formation of gas phase atoms. When aluminum is added to a flame of hydrogen + oxygen + nitrogen, it can be expected to be present as oxides, hydroxides, and hydrides, i.e., Al, AlH, AlO, AlOH, HAlO, AlO₂, Al₂O, Al₂O₂, H₂AlO, HAlOH, OAlOH, $\text{Al}(\text{OH})_2$, Al₂O₃, H₂AlOH, HAl(OH)₂ and $\text{Al}(\text{OH})_3$ —in all, 16 species. These uncharged aluminum species can be described by the general formula $\text{M} = \text{Al}_\alpha\text{O}_\beta\text{H}_\gamma$, where α , β , and γ represent the number of atoms of Al, O, and H, respectively, in the molecule, M. The enthalpies of formation at 0 and 298 K for M can be written

$$\Delta_f H_{0\text{ K}}^0(\text{M}) = \alpha \Delta_f H_{0\text{ K}}^0(\text{Al}) + \beta \Delta_f H_{0\text{ K}}^0(\text{O}) + \gamma \Delta_f H_{0\text{ K}}^0(\text{H}) - \Sigma D_0,$$

$$\begin{aligned} \Delta_f H_{298\text{ K}}^0(\text{M}) &= \Delta_f H_{0\text{ K}}^0(\text{M}) \\ &+ [H_{298\text{ K}}^0(\text{M}) - H_{0\text{ K}}^0(\text{M})] \\ &- \alpha [H_{298\text{ K}}^0(\text{Al}) - H_{0\text{ K}}^0(\text{Al})] \\ &- \beta [H_{298\text{ K}}^0(\text{O}) - H_{0\text{ K}}^0(\text{O})] \\ &- \gamma [H_{298\text{ K}}^0(\text{H}) + H_{0\text{ K}}^0(\text{H})]. \end{aligned}$$

Here ΣD_0 is the molar enthalpy of atomization of M. In the last equation, the heat correction, i.e., $[H_{298\text{ K}}^0(\text{M}) - H_{0\text{ K}}^0(\text{M})]$, for $\text{M} \equiv \text{Al}_\alpha\text{O}_\beta\text{H}_\gamma$ is calculated using the results of G3//B3LYP calculations; the corrections for the atoms of Al, O, and H again refer to the standard state and were taken from the JANAF tables [6,8]. The thermodynamic properties of each species at elevated temperatures are calculated below using a simple cycle.

Starting with the published standard enthalpies and entropies for O₂, H₂, and metallic Al at 298 K

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