

# Evaluation of Lithium Compounds as Color Agents for Pyrotechnic Flames

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## ABSTRACT

*The obstacles to producing red colored pyrotechnic flames with lithium compounds are discussed. The principle emitter of red light in such flames is atomic lithium. Hydrogen and halogens in the flame gases are expected to have a substantial effect on the concentration of atomic lithium. The development of effective Li-based red color compositions therefore depends primarily on the proper control of the concentrations of hydrogen and halogens in the flame to maximize the formation of atomic Li. Some possible ways of doing this are proposed and are supported by thermodynamic calculations.*

**Keywords:** lithium, pyrotechnics, red flame, color agent

## Introduction

Strontium and calcium compounds yield red to orange-red pyrotechnic flames. The mechanisms leading to these colors have been described in great detail by Shimizu<sup>[1a,2]</sup> and Douda,<sup>[3,4]</sup> SrCl, SrOH, CaO, and CaCl are the main species responsible for emission in the red and orange-red regions of the visible spectrum. For as long as pyrotechnists have composed new for-

mulas to generate red flames, the possibility of using materials other than strontium has been discussed. Although it would be advantageous to substitute the relatively expensive strontium with calcium, calcium-containing compositions yield a yellowish red that is much less useful than the purplish red of strontium.

Several other elements have been reported to yield a red flame color when introduced into the flame of a laboratory burner. These elements are listed in Table 1.

Radium is known to display a beautiful carmine flame, which can be attributed to the molecular emission of both monochloride and hydroxide,<sup>[5a]</sup> but the radioactivity of radium obviously prohibits its application as a flame colorant. Despite its radioactivity, the low natural abundance makes radium very expensive and thus would certainly rule out any application in pyrotechnics. The rare earth elements have been recently proposed to be potentially useful as color agents.<sup>[6]</sup> Among these, yttrium (Y), neodymium (Nd), praseodymium (Pr), scandium (Sc), and samarium (Sm) show molecular (monoxide) emission in the red region of the spectrum. Unfortunately, the most promising of these elements (Y and Sm) are expensive compared to strontium and calcium compounds. (The cost of (Sm(ClO<sub>4</sub>)<sub>3</sub>) is US\$5/g and that of

**Table 1. Elements that Display Red Flame Colors and the Color-Emitting Species.**

Element	Emitter	Main lines (nm)	Reference
Radium	RaCl, RaOH	676, 650	5a
Yttrium	YO	603, 607	6, 12c
Neodymium	NdO	650, 658, 660, 663	12c
Praseodymium	PrO	680–710 (broad)	12c
Scandium	ScO	603–636 (broad)	12c
Samarium	SmO	651, 652	6, 12c
Lithium	Li	610, 670	3

Y(NO<sub>3</sub>)<sub>3</sub>·4H<sub>2</sub>O is US\$10/g). Even as industrial chemicals, they are still fairly expensive, for example, 5 kg lots can be found for:

99.5%	Y	US \$146
99.9%	Y	US \$152
99.9%	Y <sub>2</sub> O <sub>3</sub>	US \$ 79.50
99%	Sm	US \$120

In addition, these chemicals are toxic, which makes them unattractive for practical applications.

In contrast, lithium compounds are readily available, relatively economical, and show only moderate effect on either health or the environment compared to yttrium and samarium. Lithium should be a promising substitute for strontium in red pyrotechnic flames. The low atomic mass of lithium should be an advantage in items where the weight of the composition needs to be kept as low as possible. An additional advantage is the atomic/molecular weight of the corresponding emitters. Whereas SrCl—the main emitter in the red—has a molecular weight of 123.07, the atomic weight of lithium is only 6.94. This at first glance calls (regardless of any comparison of the respective emission intensity) for an increase of specific intensity (J·g<sup>-1</sup>·sr<sup>-1</sup>) by a factor of 17 changing from strontium to lithium. Although no exact data on specific emission intensity values for SrCl and Li are available, threshold values for the visible detection of the respective color have been reported.<sup>[18,28]</sup>

When applying a SrCl<sub>2</sub> solution to a lab burner, amounts as low as 2.4×10<sup>-8</sup> g (SrCl) are said to be detectable. This corresponds to 1.94×10<sup>-10</sup> moles of SrCl. In contrast, when applying LiCl to lab burner flames, amounts as low as 1.5×10<sup>-9</sup> g (Li) are said to be visible with the naked eye, which corresponds to

2.16×10<sup>-10</sup> moles of Li.<sup>[18,28]</sup> Thus, substitution of strontium by lithium as the desired emitter in any yet hypothetical formulation would cause a reduction in weight of the color agent by a factor of about one-tenth.

## Lithium in Flames

Most chemists know that lithium compounds yield a bright scarlet flame color, similar to that produced by strontium compounds. Unfortunately, the author has not yet found any useful pyrotechnic composition showing that effect. However, most chemical reference books, as well as some monographs on energetic materials, assert the application of lithium nitrate, lithium chloride or lithium carbonate in pyrotechnics for scarlet colored flares and stars.

Although Jennings-White<sup>[7,8]</sup> gave details of a “pink” lance and of a strobe composition consisting of lithium perchlorate (LiClO<sub>4</sub>) and hexamine (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>), there is no indication of why only a pink—instead of a scarlet—flame color is obtained with these formulations. In addition, Chavez and coworkers<sup>[9]</sup> reported recently a “pumpkin orange” flame (with color values  $x = 0.534$ ,  $y = 0.398$ ) upon combustion of a composition made of ammonium perchlorate, dihydrazinotetrazine (DHT) and lithium carbonate (see Table 2).

In contrast to these disappointing attempts, combustion of several lithium compounds: (LiAlH<sub>4</sub>, LiBH<sub>4</sub>, LiC<sub>2</sub>H<sub>5</sub>) in air,<sup>[10a]</sup> as well as combustion of volatile lithium salts in methanol,<sup>[11]</sup> yield beautiful scarlet colored flames. These experiments, although not involving pyrotechnic compositions, indicate the appropriate chemistry to obtain scarlet flames with lithium.

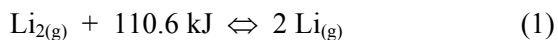
**Table 2. Lithium Compounds in Pyrotechnic Formulations.**

Application	Weight Percent				
	LiClO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>	DHT	Li <sub>2</sub> CO <sub>3</sub>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>
Lance	75	—	—	—	25
Star	—	49.5	49.5	1.0	—
Strobe lance	50	—	—	—	50

## Discussion

Introducing a lithium salt solution into the flame of a laboratory burner yields a red flame, which is due to the emission lines given in Table 1. These emissions originate from radiative transitions of gaseous atomic lithium. The main line at 670.8 nm corresponds to a  $2s^2S_{0/2}$  (ground level) –  $2p^2P_{0/2,1/2}$  (two energetically similar excited levels)<sup>[12a]</sup> transition as shown in Figure 1. (The ordinate gives the corresponding energy in units of eV; IP designates the ionization potential.)

In addition to atomic emission, lithium dimers exhibit a series of line emissions from 769.0 to 665.9 nm with the strongest line at 688.4 nm.<sup>[5b]</sup> In flame gases, however, lithium vapor is only 1%  $Li_2$  and 99% atomic lithium according to equation 1,<sup>[13a]</sup> so that the contribution of the  $Li_2$  emission to the red flame color would be negligible.



In common pyrotechnic flames these lines are superimposed on a continuum starting at 280 nm with a maximum at 400 nm, which interferes with color purity.<sup>[12b]</sup> This continuum is due to emission by  $LiOH_{(g)}$  as shown in equation 2.<sup>[14]</sup>



Ubiquitous  $H_2O$  molecules thus scavenge lithium atoms to give thermodynamically stable  $LiOH_{(g)}$ .

Sodium's atomic emission is responsible for the bright yellow flame in illuminating flares and torches, but the above effect has only a minor consequence on color purity. In contrast to equation 2, sodium (equation 3) follows a different process.



This reaction has no effect on color purity since the thermal stability of  $NaOH$  is much lower compared to  $LiOH$ , which gives rise to only trace amounts of  $NaOH$  in sodium flames. Table 3 lists the dissociation energies for gaseous alkali metal hydroxide ( $MOH$ ) decomposition according to equation 4.<sup>[15a]</sup>

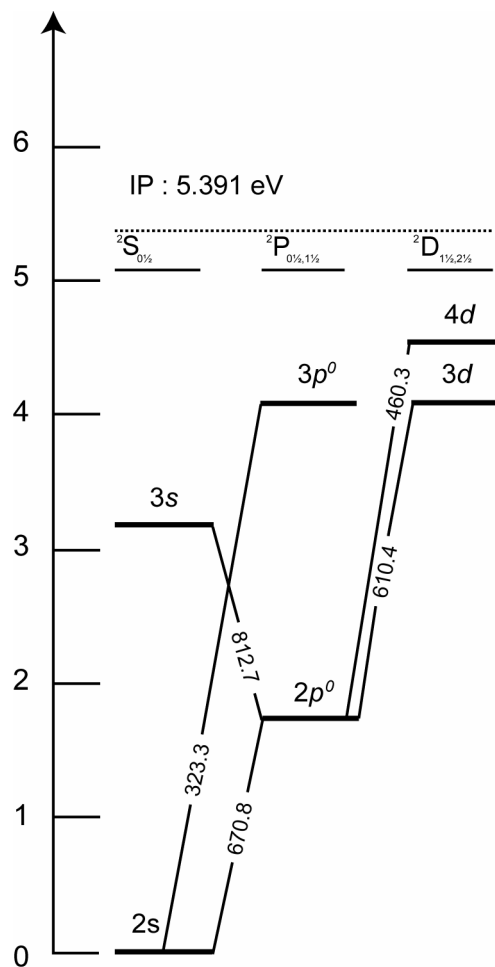


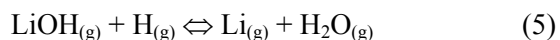
Figure 1. Atomic term diagram for lithium.

Table 3. Dissociation Energies for Gaseous Metal Hydroxides ( $MOH_{(g)}$ ).

Element	Dissociation Enthalpy of $MOH_{(g)}$ (kJ/mol)
Lithium	423
Sodium	322
Potassium	339
Rubidium	347
Cesium	381

As a consequence,  $LiOH_{(g)}$  formation in pyrotechnic flames has to be inhibited to obtain maximum atomic emission.

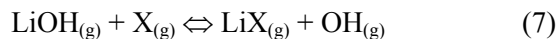
It is known that the hydrogen content of flames can be determined via evaluation of Li emission intensity.<sup>[15c]</sup> In view of this, the amount of gaseous LiOH should be reduced by the introduction of hydrogen, following equation 5,<sup>[16a]</sup> that is the reverse of equation 2.



Another disturbing effect on red flame color in lithium flames is the presence of halogens, especially chlorine. From the standpoint of oxygen content, lithium perchlorate ( $\text{LiClO}_4$ ) is superior to any other oxidizer (60.15% oxygen by weight is available for oxidation).<sup>[17]</sup> Nevertheless, flame color with  $\text{LiClO}_4$  is only pale pink as has been stated above. In contrast to barium, strontium and calcium, which, in the presence of chlorine or bromine, produce relatively stable monohalide molecules that respectively emit bands in either green, red or orange-red regions of the spectrum, halogens suppress the lithium flame spectrum as has been stated in reference 18. This effect is due to the formation of lithium chloride according to equation 6, in which X is a halogen.



Lithium chloride (as well as the other halides of lithium) exhibit no lines in the visible range but show strong continuum emission with superimposed bands at 281, 285 and 290 nm.<sup>[5c]</sup> It is interesting to note that LiF has been reported to yield a bluish glow in flames, which should originate from C-type chemiluminescence,<sup>[18]</sup> but at present it is not known if this effect could be exploited pyrotechnically. It has been explained that the introduction of halogens or their precursors in lithium-containing flames depletes the LiOH content due to the reaction given in equation 7.<sup>[16b]</sup>



The ratio of  $\text{LiOH}_{(g)}/\text{Li}_{(g)}$  itself is not changed by this reaction, but the amount that may be shifted to atomic lithium is irretrievably reduced. Thus, color purity is reduced. These findings explain the unsuccessful attempts to obtain red colored flames with traditionally formulated compositions containing lithium compounds and chemically bound halogens.

## Consequences

Any discussion of the flame chemistry of lithium would be incomplete without an attempt to find a practical approach to using lithium compounds to give a red color in fireworks or even signaling applications.

The relationship between the hydrogen content of a flame and intensity of atomic emission calls for hydrogen-rich flames. Atomic hydrogen concentration is highest in flames with a less than stoichiometric oxygen/hydrogen ratio.<sup>[15b]</sup> Thus the application of hydrogen rich fuels should be helpful in obtaining strong  $\text{Li}_{(g)}$  emission.

Since lithium perchlorate and also ammonium perchlorate are common oxidizers due to their readiness to yield oxygen in fireworks and pyrotechnics, a method should be found to prevent the scavenging of atomic lithium by the chlorine contained in these compositions.

Introduction of aluminum, preferably chemically bound (as in  $\text{Al(OR)}_3$ , where R, is an alkyl) could act as a color intensifier. Aluminum compounds are preferred over elemental aluminum since the volatility of compounds, especially metal-organic compounds, provides vaporization of aluminum within the combustion zone where it has to be supplied for further reaction with abundant halogens. With elemental aluminum, in contrast, solid-state oxidation is known to occur, which would lead mainly to a sparking flame.

Aluminum monoxide, AlO, is the main emitter in Al-containing flames, and it displays only weak continuum and spectral lines at 465, 484 and 708 nm.<sup>[1b]</sup> This is in contrast to MgO, which shows a strong continuum and thus enhances light output.

The emitters responsible for red, green and blue colors—in traditional pyrotechnic flames—are SrCl, BaCl and CuCl, respectively. These unstable compounds exist in equilibrium with the corresponding free atoms. In the presence of aluminum, chlorine is scavenged to yield  $\text{AlCl}$ .<sup>[19]</sup> This is easily explained by comparing the dissociation enthalpies of both AlCl and the previously mentioned monochlorides.<sup>[19]</sup>

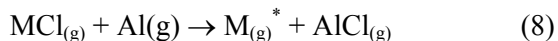
$\Delta H_D$ : AlCl: 511 kJ·mol<sup>-1</sup>

$\Delta H_D$ : SrCl: 406 kJ·mol<sup>-1</sup>

$\Delta H_D$ : BaCl: 436 kJ·mol<sup>-1</sup>

$\Delta H_D$ : CuCl: 383 kJ·mol<sup>-1</sup>

The higher dissociation enthalpy for the Al-Cl bond gives rise to the preferential formation of AlCl according to equation 8.



where M\*, is excited Ba, Cu or Sr. Consequently, the presence of Al in the flame would reduce the concentration of the MCl molecules and thus suppress the emission of the desired colored light.

In the case of lithium, however, the presence of Al is beneficial. Lithium chloride, as with the monochlorides of Ba, Cu and Sr, has a lower dissociation enthalpy than AlCl, causing aluminum to react with gaseous LiCl to release free Li atoms.

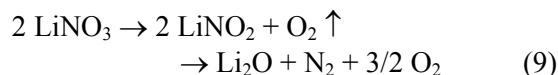
$\Delta H_D$ : LiCl: 469 kJ·mol<sup>-1</sup>

In addition, AlCl displays only lines in the ultraviolet at 261, 265 and 268 nm and no lines or continua in the visible.<sup>[20]</sup> It is not, therefore, expected to have any detrimental effect on the color purity of the flame. Similarly other elements showing  $\Delta H_D$  values for their monochlorides higher than that of LiCl, and having no—or only weak—bands in the visible should be practical scavengers for Cl in Li-containing flames (e.g., ZrCl, with weak emission at 400–415 nm).<sup>[19,24]</sup>

### Thermal Behavior of Lithium Compounds Suitable for Pyrotechnical Applications

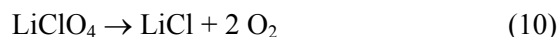
In an effort to steer the development of pyrotechnics away from intuition and towards a more scientific approach, the thermal behavior of lithium compounds will now be discussed. Unless otherwise stated, the discussion will focus on the properties of the anhydrous species.

a) Lithium nitrate (LiNO<sub>3</sub>), upon thermal treatment decomposes according to equation 9



Lithium nitrate melts at 255 °C. Decomposition starts at 365 °C as slight bubbles evolve. At 472 °C the oxygen partial pressure (p(O<sub>2</sub>)) equals 1 atm (101.3 kPa).<sup>[13b]</sup> Ellem<sup>[10b]</sup> summarized the heat of combustion for various LiNO<sub>3</sub>/fuel mixtures. Li<sub>2</sub>O, the main combustion product of such nitrate/fuel mixtures melts at 1570 °C. Its fugacity (vapor pressure) becomes 1 atm (101.3 kPa) at 2563 °C.<sup>[21]</sup>

b) Lithium perchlorate (LiClO<sub>4</sub>·3H<sub>2</sub>O) loses 2 moles of H<sub>2</sub>O between 60 and 148 °C; upon further heating, between 148 and 250 °C the last H<sub>2</sub>O molecule is released. Oxygen evolution starts at 310 °C, and the exothermal decomposition starts at 474 °C, according to equation 10.



Melting occurs at 596 °C.<sup>[27]</sup> The anhydrous salt melts at 236 °C and decomposes according to equation 10 at 440 °C. Ellem<sup>[10b]</sup> summarized the heat of combustion for various stoichiometric LiClO<sub>4</sub>/fuel mixtures.

c) Lithium pentandionate (Li(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)) is as yet a hypothetical fuel. It has been shown that the pentandionates of copper, strontium, barium, molybdenum, lanthanum, zirconium<sup>[22]</sup> and cerium<sup>[23]</sup> are suitable to impart blue, red, green, citron, pale white, dazzling white and orange colors to pyrotechnic flames in mixtures with ammonium perchlorate (AP). Since the pentandionate ligand has a large hydrogen surplus, lithium pentandionate should act as both a flame color agent and as a flame deoxidizer. Nevertheless, lithium pentandionate would require either a chlorine-free oxidizer such as TMAN (tetramethyl ammonium nitrate) or if AP were used as the oxidizer, a suitable chlorine scavenger would need to be included in the composition.

Lithium pentandionate melts at 250 °C and would presumably break down at higher temperatures to release pyrolysis products of the organic ligand including CO and alkyl fragments.

**Table 4. Stoichiometry of Compositions Investigated.**

Composition	Weight Percent					
	LiClO <sub>4</sub>	Al	NH <sub>4</sub> ClO <sub>4</sub>	Mg	Li <sub>2</sub> CO <sub>3</sub>	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub>
I <sup>[8]</sup>	50	—	—	—	—	50
II	33	34	—	—	—	33
III	33	—	—	34	—	33
IV	—	—	40	35	25	—
V	—	35	40	—	25	—

d) Lithium carbonate (Li<sub>2</sub>CO<sub>3</sub>) is an anhydrous lithium salt. It melts at 723 °C and decomposes at 1300 °C to give CO<sub>2</sub> and lithium oxide. Application of lithium carbonate as a color agent should require both high flame temperature and excess fuel to promote the formation of atomic lithium by decomposition and reduction. As lithium carbonate is a strong base (pH 11), it is incompatible with aluminum fuel.

e) Lithium oxalate (Li<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) is a colorless, anhydrous crystalline substance that is soluble in water and decomposes at 590 °C according to equation 11 to give lithium carbonate whose further decomposition was described in (d).



f) Lithium fluoride (LiF) is a colorless, crystalline, toxic substance that is slightly soluble in water and acids, melts at 845 °C, and boils at 1680 °C. It has a substantial vapor pressure at temperatures >1100 °C.

g) Lithium benzoate (C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>Li) is a colorless crystalline substance that melts at temperatures >300 °C. Its metal content is very low compared to the other lithium salts mentioned (5.42%).

Although complex lithium hydrides such as LiAlH<sub>4</sub> and LiBH<sub>4</sub> are reported to give a beautiful red color upon combustion, their sensitivity towards moisture makes them too dangerous to be handled as color agents.

It is noteworthy to mention that even elemental lithium has found application in pyrotechnics. A disclosure on IR decoy flares asserts a composition consisting of hollow PTFE blocks filled with granular lithium.<sup>[29]</sup> It seems at least that the low volume-to-surface ratio of coarse lithium prevents oxidation of the complete lithium. Although no stoichiometric proportions are

given in the disclosure, a lithium-rich composition should be feasible in terms of yielding both a high burn rate and a high specific IR intensity. At  $\xi(\text{Li}) = 0.42$ , the maximum Li<sub>(g)</sub> mole fraction in the combustion products is attained.<sup>[25]</sup>

### Thermodynamic Calculation

To prove the prediction that aluminum should act as a beneficial additive to pyrotechnic compositions, thermodynamic calculations<sup>[25]</sup> were performed on the strobe system given by Clive Jennings-White<sup>[8]</sup> and on compositions containing either aluminum or magnesium. Although lithium carbonate and aluminum are known to be incompatible chemicals<sup>[26]</sup> due to the alkaline decomposition of aluminum, calculations were performed with Li<sub>2</sub>CO<sub>3</sub>/aluminum/ammonium perchlorate mixtures to confirm the capability of strong reductive fuels to yield elemental lithium from lithium carbonate and demonstrate the suppression of LiCl formation by aluminum. All stoichiometries are given in Table 4.

The mole fractions of the relevant combustion products (the sum does not add up to 1) are listed in Table 5. Composition I displays the major combustion products for the composition given by Clive Jennings-White. It is clear that almost all of the lithium is converted to LiCl, which does not emit in the visible region. Only trace amounts of elemental lithium are formed. This explains the observed pale pink color of the flame of this composition.

The addition of equivalent weight amounts of aluminum to Clive Jennings-White's composition, as shown in composition II, results in the formation of substantial amounts of elemental

**Table 5. Mole Fractions of Relevant Combustion Products.**

Composition	H <sub>2</sub>	H <sub>2</sub> O	Li	LiCl	LiOH	MgCl	AlCl	CO
I <sup>[8]</sup>	0.39965	0.00048	0.00003	0.04162	0.00004	—	—	0.35189
II	0.31870	—	0.03097	0.03976	0.00001	—	0.03153	0.26913
III	0.28125	0.00001	0.00266	0.05829	—	0.00122	—	0.13730
IV	0.04523	0.09673	0.03374	0.09539	0.07086	0.00134	—	0.07940
V	0.14580	0.02733	0.11372	0.11258	0.02257	—	0.00439	0.12325

lithium as well lithium chloride. LiOH is only present in minor amounts. Using magnesium instead of aluminum (composition III) results in one-tenth the concentration of lithium and a correspondingly larger amount of LiCl.

With lithium carbonate as a color agent, the composition with magnesium yields substantial amounts of lithium but twice as much color-interfering LiOH (composition IV). By using aluminum instead (composition V) a very high amount of elemental lithium is formed, with only a fifth as much LiOH.

### Summary

Making effective lithium-based pyrotechnic red flames should not be “far from easy”, as Jennings-White assumed.<sup>[7]</sup>

Several rules must be obeyed to make a successful lithium red composition. These are:

- The stoichiometric ratio of oxygen to hydrogen must not exceed 1.0 to favor H<sub>2</sub>O dissociation to atomic hydrogen. To accomplish this:
  - Use fuels with high hydrogen content
  - Make the stoichiometry fuel rich; in other words, avoid an oxygen surplus
- Halogens should be avoided
  - If halogens cannot be avoided, aluminum should be added to scavenge the halogen
  - Each lithium compound has to be treated differently to obtain maximum color purity

Although only theoretical evidence has been given for this hypothesis, it is hoped that an experimental proof will be found soon.

A remaining problem with many lithium compounds is their high hygroscopicity, which will make practical applications difficult.

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