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Comment

Comment on “Influence of the radical size  
on the  $\text{Ca}^* + \text{ROH} \rightarrow \text{CaOH}^* + \text{R}$  ( $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$  and  $\text{C}_3\text{H}_7$ )  
reaction cross section”

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**Abstract**

The recent results of Esteban, Garay, García-Tijero, Verdasco and González Ureña reexamined in the light of previous investigations on the same class of reactions.

In the title Letter [1], Esteban et al. have reported reactions of electronically excited ( $3s4d\ ^1D_2$  and  $3s3p\ ^3P_j$ ) calcium atoms, with a variety of alcohols (methanol, ethanol and *n*-propanol). The reactions were investigated under beam-gas conditions. The only chemiluminescence signal that was observed originated from the  $A\ ^2\Pi$  and  $B\ ^2\Sigma$  states of calcium monohydroxide, CaOH. The chemiluminescence cross section is very small, of the order of  $10^{-3}$  to  $10^{-2}\ \text{\AA}^2$ .

These results are intriguing, since they are at odds with the already known gas-phase chemistry of the alkaline earth elements.

The chemistry of alkaline earth alcohol mixtures has been investigated both in the single collision [2,3] and in the multiple collision [4] regimes with special emphasis on the reactions of barium atoms. In reactions of methanol, both with ground state ( $6s^2\ ^1S_0$ ) and metastable ( $6s5d\ ^1D_2$ ) barium atoms, only the  $\text{BaOCH}_3 + \text{H}$  exit channel was observed, despite the much larger exoergicity for formation of

either  $\text{BaOH} + \text{CH}_3$  or  $\text{BaO} + \text{CH}_4$ . These observations have suggested that the formation of the reaction products results from a migration of the H atom that is bonded to oxygen, a process that is strongly enhanced by electronic excitation of the incoming barium atom [2]. Similar results have been reported by de Pujo et al. [3] in an investigation of chemiluminescence in  $\text{Ba}(6s6p\ ^1P_1)$  reactions with water, alcohols and ethers. Here again, migration of the H atom that promotes the insertion of Ba into the OH bond of the alcohol group was the key step in the reaction mechanism. Finally, Brazier et al. [4] have investigated the reactions of calcium, strontium and barium with methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, acetone and acetaldehyde. Once again, the only chemiluminescent product observed in reactions with the alcohols is the alkaline-earth alkoxide, MOR ( $M = \text{alkaline earth}$ ,  $R = \text{alkyl radical}$ ).

The Letter of Esteban et al. [1] is surprising since no previous study reports the observation of an

Table 1  
Energetics of the Ca + CH<sub>3</sub>OH system

Reaction	$\Delta H$ (eV)
Ca( <sup>1</sup> D <sub>2</sub> ) + CH <sub>3</sub> OH → CaOH(A) + CH <sub>3</sub>	-1.0
Ca( <sup>1</sup> D <sub>2</sub> ) + CH <sub>3</sub> OH → CaOH(B) + CH <sub>3</sub>	-0.8
Ca( <sup>1</sup> D <sub>2</sub> ) + CH <sub>3</sub> OH → CaOCH <sub>3</sub> (A) + H	-0.4
Ca( <sup>1</sup> D <sub>2</sub> ) + CH <sub>3</sub> OH → CaOCH <sub>3</sub> (B) + H	-0.2
Ca( <sup>3</sup> P <sub>J</sub> ) + CH <sub>3</sub> OH → CaOH(A) + CH <sub>3</sub>	-0.2
Ca( <sup>3</sup> P <sub>J</sub> ) + CH <sub>3</sub> OH → CaOH(B) + CH <sub>3</sub>	+0.1
Ca( <sup>3</sup> P <sub>J</sub> ) + CH <sub>3</sub> OH → CaOCH <sub>3</sub> (A) + H	+0.4
Ca( <sup>3</sup> P <sub>J</sub> ) + CH <sub>3</sub> OH → CaOCH <sub>3</sub> (B) + H	+0.6

alkaline-earth hydroxide by reaction with alcohols. The only work so far where alkaline-earth hydroxides have been observed, often together with the oxides and the alkoxides, is when the molecule that reacts has a clear OH leaving group, as is the case with water [2,5] and alkyl hydroperoxides [6].

The work of Esteban et al. needs to be discussed in detail in order to see whether it can fit with the picture of the alkaline earth/alcohol reactions discussed above, or whether it is in conflict with it. Unfortunately, such a discussion cannot be found in the Letter of Esteban et al. [1].

In fact the situation is simple if one considers the energetics of the calcium-methanol reactions listed in Table 1. The bond strengths used to construct the table are taken from Ref. [7] (CH<sub>3</sub>-OH and CH<sub>3</sub>O-H) and Ref. [8] (Ca-OH). The unknown Ca-OCH<sub>3</sub> bond strength was taken to be equal to that of Ca-OH. The energy of the relevant electronically excited levels are taken from Ref. [9] for Ca, and from Ref. [4] for CaOH and CaOCH<sub>3</sub>.

Examination of Table 1 shows that the only chemiluminescent channel that is open for the reaction of Ca(<sup>3</sup>P<sub>J</sub>) is the formation of CaOH(A), and also that of CaOH(B) if the collision energy (0.14 eV) available in the Ca-CH<sub>3</sub>OH experiment of Esteban et al. is included. For the reaction of Ca(<sup>1</sup>D<sub>2</sub>) fluorescent emission from both CaOH and CaOCH<sub>3</sub> could be observed. However, de Pujo et al. [3] have shown that the bond energy of Ba-OCH<sub>3</sub> is substantially smaller than that of Ba-OH (3.8 versus 4.6 eV). If the same situation is encountered with calcium, then the production of electronically excited CaOCH<sub>3</sub> is also energetically closed for reaction of Ca(<sup>1</sup>D<sub>2</sub>), as is the case for reaction of Ca(<sup>3</sup>P<sub>J</sub>).

From these energetic considerations, it is thus not surprising that the chemiluminescence observed in the work of Esteban et al. originates from CaOH. Now, let us take into consideration the reaction mechanism discussed above for the alkaline earth/alcohol reactions. The reaction involves an H-atom migration that eventually produces CaOCH<sub>3</sub> as the major product. We conclude that if CaOH is formed in the reaction it can only correspond to a minor reaction product, a fraction of which is electronically excited. This conclusion agrees with the small chemiluminescent cross sections reported by Esteban et al. for the reaction of calcium with methanol. A similar picture holds for the other alcohols investigated by Esteban et al. [1].

Why was the minor hydroxide channel not observed in Refs. [3,4]? There are two main reasons: firstly, the energetics in those cases did not preclude the chemiluminescent emission of the major alkoxide product, and secondly the emission spectra of electronically excited calcium hydroxide and calcium alkoxides are close together [4]. For these two reasons, the weak chemiluminescence of CaOH, was hidden by that of the dominant calcium alkoxide product.

To confirm the present interpretation, a laser-induced fluorescence study of the ground state reaction products would be highly desirable.

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