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Artigo

THE EXTINCTION OF THE *IGNIS FATUUS*

Antonio C. Pavão[a,*], Gerson S. Paiva[a] and Cristiano C. Bastos[b]
[a]Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50740-560 Recife – PE, Brasil
[b]Departamento de Química, Universidade Federal Rural de Pernambuco, 52171-900 Recife – PE, Brasil

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Ignis fatuus, a luminous phenomenon witnessed over the centuries by observers around the world, is no longer seen in modern times, suggesting that it is extinct. An explanation for this disappearance can be found in the description of *ignis fatuus* as a cool flame of methane. Unlike a conventional flame, which generates large amounts of heat, *ignis fatuus* is a flame that glows without heat through a chemiluminescence process. Its characteristic bluish color is due to the emission of excited formaldehyde, which is formed in the slow combustion of methane. It is generally accepted that the phenomenon is a spontaneous combustion of swamp gas in contact with the oxygen in air, but an analysis of the energies involved in the cool flame process indicates that the phenomenon is not spontaneous in nature. Experiments carried out in the 19th century show torches being used to ignite *ignis fatuus*. The abandonment of fire in favor of night lighting may hold the secret to this mystery of *ignis fatuus*'s extinction.

Keywords: *ignis fatuus*, will-o'-the-wisp; methane; cool flame.

INTRODUCTION

Ignis fatuus, *Will-o'-the-Wisp*, *Jack-o'-Lantern*, *Shui têng, Hitodama*, and *Boitatá* are just a few of the names used to denominate a luminous phenomenon witnessed over centuries by observers in various parts of the world. It appears as a pale bluish flame and was generally seen at night in cemeteries and swamps and near stagnant, still waters and canals. *Ignis fatuus* is the stuff of legend and lure, striking fear in those who traveled by night, inspiring poets and artists, and sparking debate among famed scientists. Former references to *ignis fatuus* appear in Chinese literature. There are records of 'water lanterns' (*shui têng*) in the *Kuei Hsin Tsa Chih* of Chou Mi (13th century), Li Shih-Chen (+1596) calls it 'yang flames of marshes', and lights in the water are reported in *Shan Thang Sio Khao* by Phêng Ta-I (+1595).[1] It also appears in the works of William Shakespeare in Henry IV,[2] Johann Goethe in *Faust*,[3] Emily Dickinson in *Those-Dying Then*,[4] Lewis Carroll in *Euclid and his modern rivals*,[5] Charlotte Brontë in *Jane Eyre*[6] and others, including the well-known stories of *Lord of the Rings* and *Harry Potter.*[7] In music, it appears in the classics, Franz Liszt in *The Transcendental Etude No 5 'Feux Follets*,[8] Franz Schubert in Winterreise,[9] and Frédéric Chopin in Étude in A Minor Op. 10, No. 2.[10] In Brazilian folklore, *ignis fatuus* has several denominations, including *João Galafoice, Cumadre Fulozinha, Mula sem Cabeça, Tocha, Fogo Corredor, Fogo Fátuo*, and *Boitatá*, this last of which is derived from the Tupi indigenous language of *mboî tatá* and means 'fire snake'. In one of his letters, the European colonizer Father José de Anchieta speaks of a 'ghost' in the form of a 'sparkling beam' that attacks the indigenous people and kills them.[11] This particular entity is a character in Brazilian folklore that defends nature against the attack of its predators.[12]

Ignis fatuus today calls our attention not due to its natural mystique, but precisely because the phenomenon is no longer witnessed. Considering how far we have come in our capacity to observe and record natural phenomena, this disappearance constitutes a mystery.[13] However, understanding *ignis fatuus* as consisting of a cool flame of methane can provide a reasonable explanation for this disappearance.

*e-mail: antonio.pavao@ufpe.br

A METHANE COOL FLAME

Meaning 'foolish fire' in Latin, *ignis fatuus* is not quite brilliant enough to illuminate its surrounding environment and glows 'without heat', as noted by Isaac Newton,[14] who distinguished the phenomenon from the flame of a candle or that of burning wood. Joseph Priestley[15] analyzed accounts of *ignis fatuus* and found that it occurred during a 'dark and calm night', emitting a 'pale inoffensive light'. In 1783, George Washington and Thomas Paine conducted an experiment in the Millstone River to prove their hypothesis that *ignis fatuus* was produced by methane emanating from swamps.[16] They held torches close to the mud, where they saw bubbles rise, at which point a flash of light broke out across the water. Similarly, Louis Blesson, the author of very detailed accounts of *ignis fatuus*, also employed torches to produce flames in the air bubbles rising from the marshes in the Gorbitz Forest, Newmark, and other localities in Germany.[17]

Swamp gas is composed of approximately two-thirds of methane,[18,19] a product that emerges from the bacterial anaerobic decomposition of cellulose and proteins in vegetation. While the combustion of methane in air generally produces hot flames, it can also produce cool flames.[20,21] Unlike conventional flames, which generate large amounts of heat, carbon dioxide, and water, cool flames result from a slow combustion process. In 1817, Humphry Davy[22] observed cool flames by inserting a hot platinum wire into a mixture of air and diethyl ether vapor. According to Davy, 'When the experiment on the slow combustion of ether is made in the dark, a pale phosphorescent light is perceived above the wire...'. Harry Emeléus[23] recorded the first emission spectrum of low intensity, low temperature flame for different fuels, which included ether, aldehydes, and hexane. Vladimir Kondratiev[24] identified the spectral bands as being identical to gas phase formaldehyde fluorescence. A cool flame can also be observed in methane under certain conditions. At atmospheric pressure, the temperature of the methane cool flame is below 475 °C, whereas the hot flame occurs from 580 °C.[25] The cool flame of methane produces excited formaldehyde, or CH_2O^*, in addition to H_2O_2 and small quantities of CO, H_2, CO_2 and H_2O.[20] In fact, the formaldehyde emission spectrum, with peaks at 350 nm and 400 nm,[23,26] corresponds to the same pale bluish color as that of *ignis fatuus*.

THE IGNITION PROBLEM

Although the methane cool flame hypothesis is quite acceptable, a major problem is related to the spontaneous ignition of swamp gas. The British geologist Alan Mills[27,28] attributed the auto-ignition of swamp gas to the oxidation of phosphine, which is produced in biodegradation processes. While phosphine is indeed present in low concentrations in swamp gas,[18,19] this theory does not explain natural ignition, since phosphine or diphosphine oxidation itself are not spontaneous in air.[29] The Italian chemists Luigi Garlaschelli and Paolo Boschetti, 'on the track of the *Will-o'-the-wisp*', successfully created a weak, cool flame by mixing phosphine with air and nitrogen in certain proportions.[30] Those cool flames were greenish in color. Therefore, they do not resemble the natural phenomenon, which emits bluish light. No other component of the swamp gas could initiate the combustion of methane. In 1776, Alessandro Volta considered the interaction between electricity and flammable air to be the master key to understanding the *ignis fatuus* phenomenon. Accordingly, such an interaction could not only give an account of the *ignis fatuus* phenomenon, but it could also explain various 'meteors'.[31] However, it is important to separate *ignis fatuus* from other cases, such as luminous meteors. Furthermore, there is no connection of the *ignis fatuus* with external sources of electricity. For a better understanding of the ignition problem, an analysis of the methane cool flame reaction mechanism was performed. The reactions involved in the cool flame of methane and the formaldehyde formation are shown in Figure 1.

The first step is the methane oxidation $CH_4 + O_2 \leftrightarrows CH_3 + HO_2$. The CH_3 radical turns into CH_3O_2 with O_2 addition, and HCO through the reaction $CH_3 + O_2 \leftrightarrows HCO + H_2O$. Due to the presence of HO_2, CH_3O_2H is produced by the reaction $CH_3O_2 + HO_2 \leftrightarrows CH_3O_2H + O_2$. The excited formaldehyde CH_2O^*, which is responsible for the blueish emission of the cool flame, is formed with the HCO addition $CH_3O_2H + HCO \leftrightarrows CH_2O + CH_3O_2$.[20] The molecular orbital calculations were performed at the Density Functional Theory (DFT) level using the hybrid functional B3LYP and employing the 6-311G basis set.[32] As simple molecules are involved in the reaction mechanism, the results obtained with this level of theory are reliable for the present purpose. The bond lengths of the molecules were taken from the experimental database.[33] The optimization of the intermediate state in each of the steps is performed by approximating the two molecules until they reach the top of the potential barrier. As shown in Fig. 1, the activation energy of the chemical reactions is more than a hundred kcal/mol (117.38 kcal mol^{-1} in the first step), corresponding to temperatures above 250 °C. This means that, in nature, an extra source of energy is needed to ignite the cool flame of methane. That is, *ignis fatuus* is not the spontaneous combustion of swamp gas, as has been argued for years.[13,27]

CONCLUSIONS

For more than a century, there have been no reliable records of *ignis fatuus* sightings like those reported in the past. Marshy grounds are no longer common on the planet, which could explain this disappearance. However, marshes are still being preserved today, and there are cemeteries and swamps where methane is naturally produced. A more adequate explanation can be found by understanding *ignis fatuus* as a cool flame of methane, a nonspontaneous phenomenon in nature, requiring it to be ignited. Washington and Paine in North America,[16] along with Blesson in Europe,[17] were successful in their efforts to employ torches that could produce these flames in the air bubbles that rise from the swamp. Their experiments were valuable in affording us some understanding of the many sightings of *ignis fatuus* in the past, when torches and lamps were commonly used to guide travelers at night through the forest. It seems that *ignis fatuus* is not the days of 'cold' lanterns, swamp landfills and light pollution. Although artificial ignition of gases by humans is a reasonable explanation, the mystery of the extinction of *ignis fatuus* may not be completely solved. Activation energies can be overcome with catalysts that exist in the air in the form of dust, microorganisms and pollutants. In cemeteries, for example, there are certain circumstances different from those in swamps that may require other chemical alternatives to explain the phenomenon. Therefore, it seems premature to proclaim

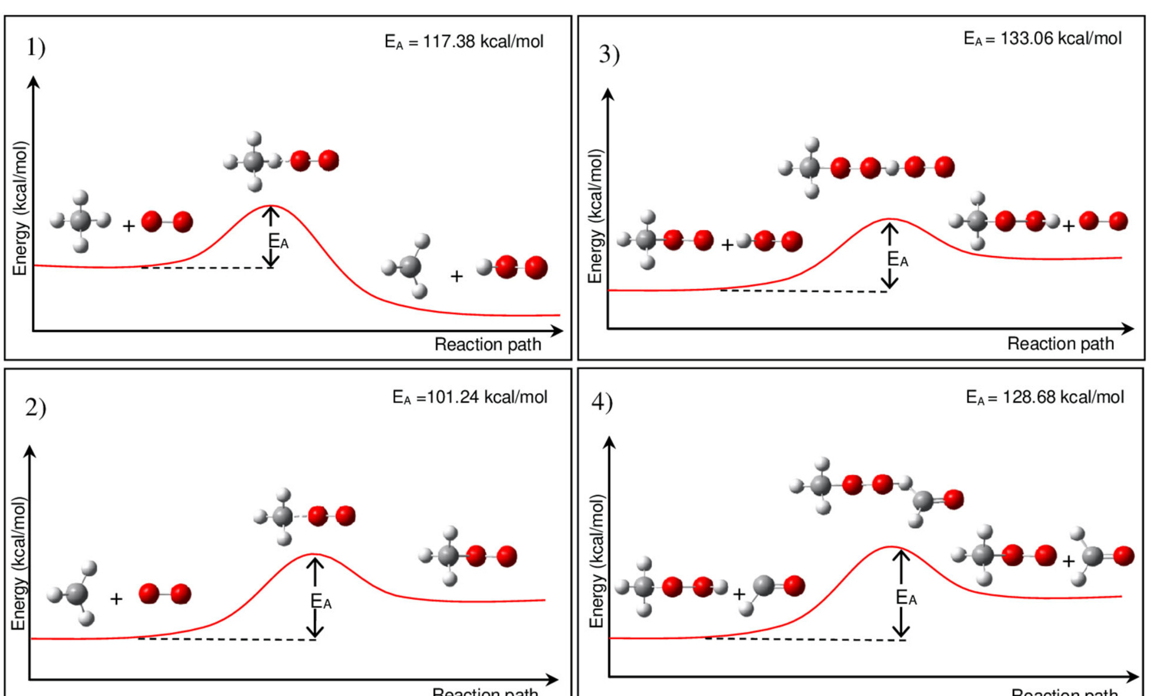

Figure 1. *Methane cool flame reaction mechanism. The excited formaldehyde (CH_2O^*), which is responsible for the blueish emission of the cool flame, is formed in the last step*

the extinction of the *ignis fatuus*. At any time, someone may, either accidentally or as planned, announce the return of *ignis fatuus*, this time no longer to fool people, but perhaps to continue to inspire artists and intrigue scientists.

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