American Journal of Chemistry 2021, 11(3): 49-51
DOI: 10.5923/j.chemistry.20211103.02

# On the Chemistry of Sonnenschein Test for Strychnine

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**Abstract** The study of the chemistry of a bioactive compound is important, the more if the substance is a violent poison. In this case chemical results are applied in forensic chemistry. The Sonnenschein test consists in the electron-transfer oxidation of strychnine, via cerium mediated radical reactions. Besides, this test produces a violet colour more stable than that obtained with potassium dichromate which is the recommended assay for identification of this drug. Since neither the chemistry nor the reaction mechanism have been advanced, we provide the electron flow, step by step, from the alkaloid to the complex oxidation product.

**Keywords** Ceroceric oxide, Ceric sulphate, Radical reactions, Reaction mechanism, Reactive intermediates

## 1. Introduction

The chemistry related to the rare –earth metal cerium is scant. However, Sonnenschein used ceroceric oxide and sulphuric acid for strychnine detection. This spot test produces an intense violet colour.

In this communication, the reactions taking place in this test are described. It is a one-electron process and we arrived, step by step, to the complex oxidation product whose structure was elucidated decades after the test was proposed.

This paper is a follow-up of other studies on reaction mechanism, [1-5].

## 2. Antecedents

The test understudy is due to the German pharmacist Franz Leopold Sonnenschein (1819-1879). He used $Ce_3O_4$ and sulphuric acid for strychnine identification. He published his test in a medical, in a pharmaceutical, and in a chemical journal, [6-8]. His work was reviewed in England, [9], and registered in the United States, as indicated [6,7].

He named the reagent Ceroxyduloxide (cerium oxydulus oxide) in reference to the lowest and to the highest oxidation states of cerium in this compound. $Ce_3O_4$ has been termed ceroceric oxide, [10], but it can be considered an oxysalt ($2CeO.CeO_2$), cerium dioxide acting as anhydride in combination with cerium monoxide (ortho-salt), in a similar manner as in minium, $Pb_3O_4$.

The Ce(II) compounds are scarce, but $CeI_2$,$Ce(OH)_2$ and CeO are known [11-13].

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Received: Jul. 15, 2021; Accepted: Jul. 28, 2021; Published: Aug. 15, 2021
Published online at http://journal.sapub.org/chemistry

The Sonnenschein test produces a blue colour more stable than that obtained with chromic acid, a method recorded in 'Modern Plant Analysis' and in 'Drug Analysis', [14,15].

The blue colour gradually turns into cherry red and then remains unchanged for several days. In terms of sensitivity even 1 μg of strychnine can still be clearly recognized.

The ceric ion is a strong oxidizer, especially under acidic conditions. When ceric compounds are reduced, cerous derivatives are formed and the orange colour of cerium(IV) ions vanishes since cerium(III) ions are colourless, [16,17].

The electronic configuration of the rare-earth metal cerium is: [Xe] $4f^1 5d^1 6s^2$, [18]. These outer electrons are mis- sing in Ce+4.

The electronic configuration of Cerium+3 is: [Xe] $4f^1$, [19].

Even though Ce+4 presents a noble gas structure, it can be reduced to Ce+3 in order to decrease the positive charge in the nucleous. Compare Kossel, [20]. Therefore, it can accept one electron in 4f subshell.

## 3. Discussion

Strychnine, Figure 1, is a seven-ring alkaloid and exhibits a lactam, a cyclic ether, a double bond, and a tertiary amine.

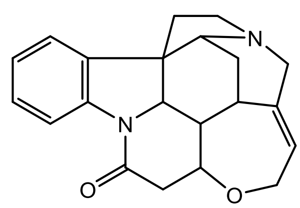


**Figure 1.** Graphic formula of strychnine

The product isolated from potassium permanganate oxidation features a carbonyl group vicinal to the tertiary nitrogen (a new lactam group). There are also a ketone and a carboxylic acid. An uptake of four oxygen atoms and loss of two hydrogen atoms has occurred, [21].

Cerium(IV) sulphate, formed in situ, is a powerful oxidant in acidic medium, and it is the reactive species in the Sonnenschein test. Since the same violet colour is produced in chromic acid test, it is expected that the resulting product in these strong oxidations will be the same. In fact, we arrived to the described oxidation product. We provide the reaction course from the alkaloid to the final product and developed the electron flow.

The first step is Ce+4 subtraction of one electron from the double bond, a preferred tertiary carbonium ion is formed and also a free radical results, Figure 2, **a**, **b**. There are four hydrogen atoms for possible elimination, two are endocyclic and two exocyclic, so the statistical factor doesn't matter. The exocyclic double bond is preferred since there can be interaction of the unshared electron pair of the nitrogen with the π electrons of the double bond, **c**. Compare to aniline, [22].

Then, removal of the free radical by Ce+4 gives a carbocation, **d**, which is neutralized by the enamine (faster internal reaction), the endocyclic double bond is restored and the resulting iminium ion reacts with water, giving a carbinol, **e**, **f**.

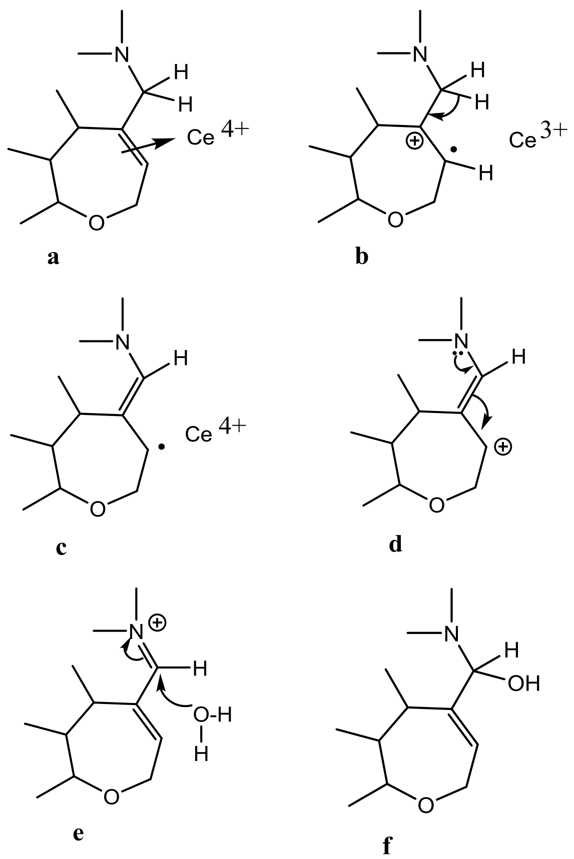


**Figure 2.** First oxidation product of strychnine

Oxidation to carbonyl forms a new lactam, **g**, a non-oxidizable carboxylic acid derivative, Figure 3.

Reaction of Ce(IV) with the double bond yields a radical vicinal to carbonyl and a secondary carbonium ion, which is neutralized by water, **h**, **i**. The free radical is steric hindered and may have resonance with the carbonyl group. Then there is Ce+4 remotion of an electron from the hydroxyl group, and the two free radicals couple to form an epoxide, **j**, **k**. Acid hydrolysis gives a vicinal diol, **l**, which is broken down by the oxidizer. There is ring opening with concomitant formation of a ketone and an aldehyde, **m**, **n**. Then, oxidation to carboxylic acid gives the multi-functional final product.

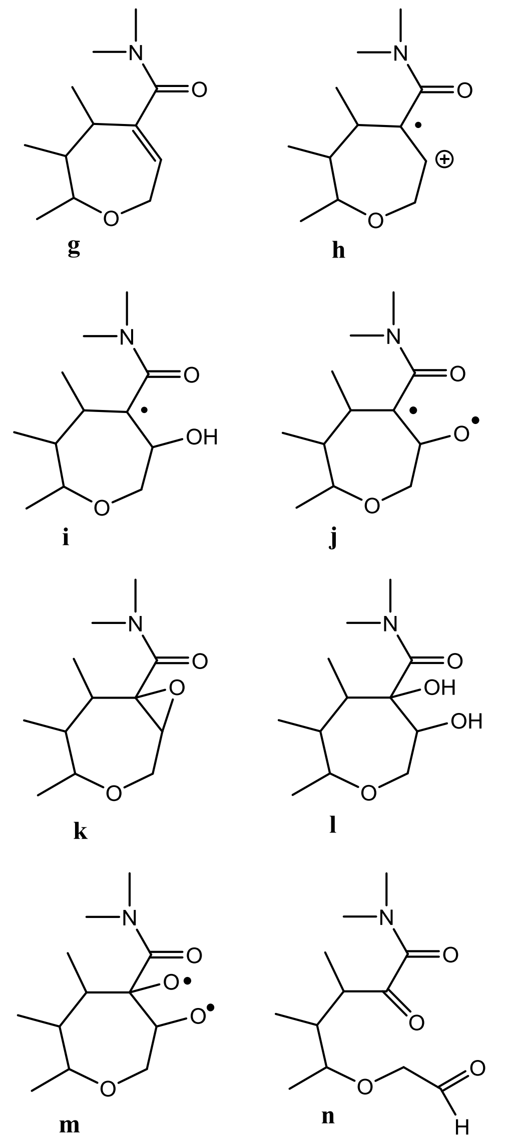


**Figure 3.** Next oxidation steps of strychnine

# 4. Conclusions

We have studied the chemistry involved in the Sonnenschein test for strychnine identification. This redox process occurs via cerium mediated radical reactions. These are: electrophilic attack to the double bond, hydrogen elimination, free radical subtraction by cerium(IV), isomerization, alcohol oxidation, carbocation neutralization by water, epoxide formation, acid hydrolysis, ring opening, and aldehyde oxidation. Some reactions are repeated.

This way the route from the alkaloid to the tetra-functional final product has been described. It is based on the reactivity of the groups present in strychnine, as well in the chemical deportment of the reagent.

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