

On the interaction of apomorphine with ammonium tellurate in acidic medium

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Magna Scientia Advanced Research and Reviews, 2026, 17(01), 308-311

Publication history: Received on 01 May 2026; revised on 08 June 2026; accepted on 11 June 2026

Article DOI: <https://doi.org/10.30574/msarr.2026.17.1.0105>

Abstract

Apomorphine is a very interesting compound, both from the chemical point of view and from the biological-medical side. Apomorphine derives from acid catalysed rearrangement of morphine. However, the reaction mechanism has not been understood even at the present, notwithstanding that a correct sequence was advanced recently, including accepted thermodynamic rules and avoiding forbidden steps by thermodynamics found in other proposals.

Apomorphine is a bioactive compound used to improve hypomobilia due to Parkinson's disease. In the present communication the chemistry of Brociner's test for apomorphine is provided, as well as the reaction mechanism. The test is based on the interaction of apomorphine with ammonium tellurate in sulphuric acid. The reactive species is protonated telluric acid generated in situ. An SN_2 reaction with a phenol group in apomorphine gives a mixed tellurate, whose interaction with a hydron produces a concerted reaction mechanism, involving a vicinal phenol group as well as a C=C double bond. Telluric acid is eliminated and an ortho-benzoquinone is formed.

Keywords: Ammonium tellurate; Concerted mechanism; Organo-metallic tellurate; Substitution reaction; Telluric acid; Telluric acid; Tellurium dioxide

1. Introduction

Apomorphine is a synthetic opioid obtained by rearrangement of morphine to apomorphine in acidic medium. A patent heats morphine in phosphoric acid in the presence of phosphorus pentoxide at 90-100° under an inert atmosphere. The solution was stirred during 2 hours. Hydrolysis of the phosphate by pH regulation, extraction of the base, and hydrochloride formation gave the pure salt, [1].

A Hungarian method uses methansulphonic acid for the microwave assisted rearrangement of morphine to apomorphine, heating at 90°C during five minutes. [2]. The yield is 73%.

The reaction mechanism has been cleared recently [3], correcting a previous one [4] provided in 1965, as well as other two proposals, [5].

Apomorphine is an antiparkinsonian drug and emetic [6]. It is indicated to treat hypomobility (movement disorders) and muscle stiffness associated with Parkinson's.

In this communication we provide the reaction mechanism of Brociner's test for apomorphine detection. It is a follow up of other similar studies, [7-11].

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2. Study Method and Process

This is an Organic Chemistry Theoretical Study. It is based on the chemical department of reagent and substrate. All is in accordance with the reaction medium and the catalyst present. The several steps leading to the final product are fully commented and the reaction mechanism is given too.

3. Antecedents

The test under study is due to Professor Alphonse Lupu Brociner, working at the Pharmacy School in Bucharest. He dissolved 1 g of ammonium tellurate in 20 ml of concentrated sulphuric acid, choosing the clear solution and leaving the insoluble part. Some salt is decomposed due to the action of the acid, with evolution of tellurated hydrogen. Apomorphine gives violet colour, [12, 13].

Tellurium atoms have 52 electrons and the shell structure is: 2, 8, 18, 18, 6. The electron configuration is: [Kr] 4d¹⁰, 5s², 5p⁴ [14]. Oxidation states: -2, +2, +4, +6. [15]. Tellurium gives a greenish blue flame when burnt in the air, dissolves in nitric acid, and is used in the manufacture of solar panels, although it is a very rare element, [16]. If someone eats a tellurium compound, it gives them garlic breath, [17].

Telluric acid is H₂TeO₄, meta-telluric acid, from which diammonium tellurate derives, [18, 19]. Other form of telluric acid is Te(OH)₆, often written as H₆TeO₆, is ortho-telluric acid. It is a weak acid and dibasic. As oxidizer it is reduced to TeO₂, [20]. Tellurium dioxide is barely soluble in water and soluble in strong acids, [20].

4. Discussion

The first step in Brociner test is interaction of ammonium tellurate with sulphuric acid, which generates meta-telluric acid and ammonium sulphate. The reactive species is protonated telluric acid. The electrodotic property [21, 22] of phenols, especially the less hindered external one in apomorphine, produce an S_N2 reaction, giving a tellurate at C-3 and elimination of water. Protonation of the organo/metallic ester produces a concerted mechanism, tellurios acid is separated and an ortho-benzoquinone is formed by participation of the vicinal phenol group and migration of the intermediate double bond. Dehydration of tellurios acid affords tellurium dioxide, soluble in the strong acidic medium.

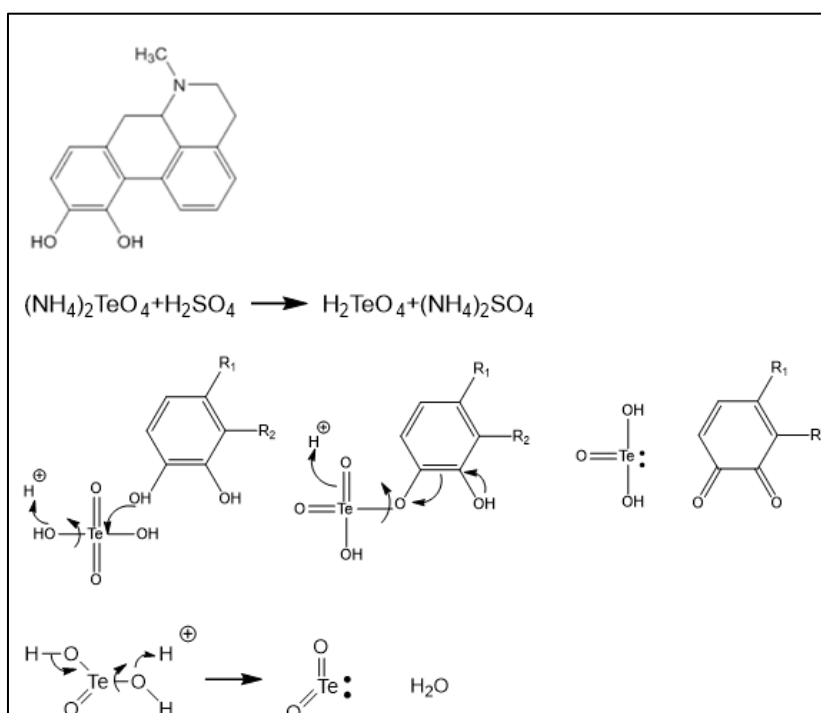


Figure 1 Oxidation of apomorphine with telluric acid

Ortho-benzoquinones are red [23], however the observed colour is violet, and since there are not tellurium blue compounds, the violet colour indicates halochromism, [24, 25].

5. Conclusion

The chemistry and the mechanism of the Brociner test for apomorphine using ammonium tellurate in sulphuric acid, have been cleared. Protonated telluric acid reacts with a phenol group in apomorphine giving a mixed tellurate whose interaction with a hydron produces a synchronous mechanism. Tellurous acid is eliminated and an ortho-benzoquinone is formed (oxido-reduction step). Dehydration of tellurous acid affords tellurium dioxide.

Compliance with ethical standards

Disclosure of conflict of interest

There is no conflict of interest to declare

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