

## On Dulcin detection by electron transfer

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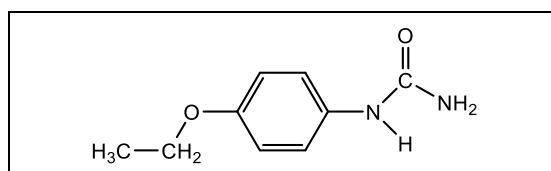
### Abstract

The artificial sweetener Dulcin has been detected by reaction with mercury nitrate (Jorissen test), with silver nitrate or with mercury chloride (Ruggeri test). With these reagents a violet colour is developed. Since there are few violet organic compounds, and these exhibit structures more complex than the expected one from Dulcin, it was pertinent direct the attention in order to clear up the chemistry involved in these assays. The reagents employed have reducible cations; thus, there must be oxidations via electron transfer. However, the Dulcin molecule does not show an adequate site for this type of reaction. Nevertheless, hydrolysis of the ureido chain in Dulcin gives 1,4-phenetidine which is suitable for electron transfer. This way organic radical cations similar to the violet Wurster's salts can be formed. These compounds are in resonance with quinonoid structures. The sui generis hydrolysis of the ureido chain is commented. This reaction and the degradation of the companion isocyanic acid occur via zwitterions.

**Keywords:** Radical cations; Reactive intermediates; Reducible cations; Ureido hydrolysis; Wurster's salts; Zwitterions

### 1 Introduction

Dulcin is a potent sweetener about 250 times sweeter than sugar. It was prepared for first time by the Polish chemist Józef Berlinerblau in 1883, [1]. This compound is p-phenetolcarbamide, Figure 1.



**Figure 1** Dulcin structure

In this communication we provide for the first time the chemistry, with the electron flow, of some tests for Dulcin detection.

This paper is a follow up of our studies on reaction mechanism, [2-6].

### 2 Antecedents

Wender published a test for Dulcin by reacting it with fuming nitric acid. After evaporation to dryness in the water bath, phenol solution and sulphuric acid are added, a blood red colour is developed. He published his test in Germany [7], and it was recorded in the same year, 1894, in the United States [8], and afterwards in a book on chemical tests, [9].

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Some years later, other tests for Dulcin detection were proposed, not by nitration and subsequent steps, but using electron capturing reagents such as mercuric nitrate, Jorissen [10, 11], and silver nitrate or mercuric chloride, Ruggeri [12, 13]. In these tests a violet colour is developed. This is interesting since there are rather few violet organic compounds and they display structures that are more complex as to be coming from a molecule like Dulcin.

In the next section we disclose the chemistry of these tests. Each step is fully commented.

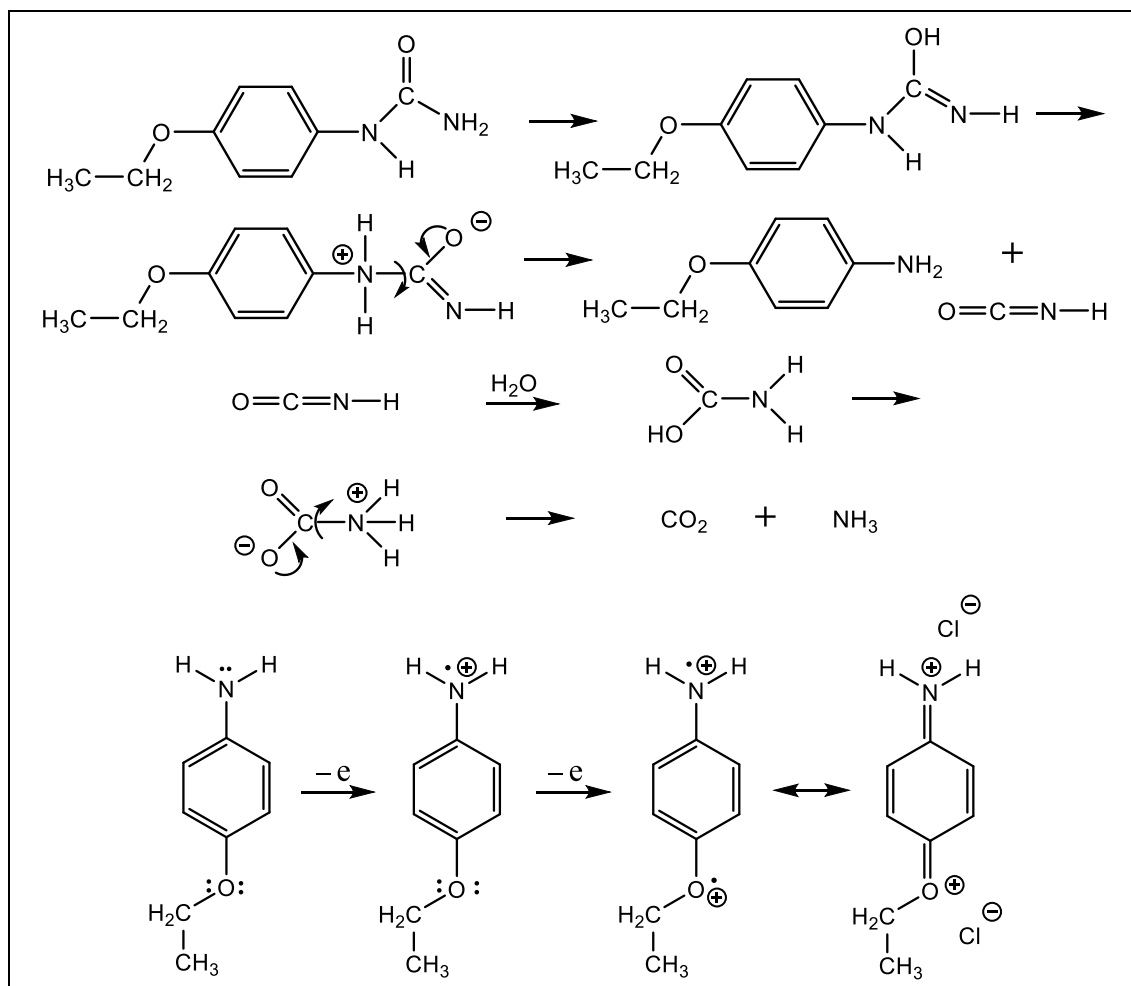
### 3 Discussion

The reagents in the Jorissen and Ruggeri tests for Dulcin are electron captor compounds, but at first glance there is no adequate site in the Dulcin molecule for this type of reaction to occur. However, hydrolysis of this ureido must yield p-phenetidine, an aromatic amine capable to be oxidized by electron acceptor reagents.

Thus, the hydrolysis of urea was revised. The mechanism of this reaction is different to the proposed for a monoamide, [14]. It is an intramolecular break down assisted by a water molecule and it is found to have the lowest activation energy. The assisting water molecule acts as hydrogen transfer. This way the imidol structure is formed, Figure 2. The hydrogen atom of this acidic enol migrates to the nitrogen atom linked to the phenyl ring, via assisting water molecule. A zwitterionic intermediate results, favouring C-N cleavage and formation of phenetidine and isocyanic acid, which readily hydrolyses to carbon dioxide and ammonia, Cf. [15].

Dulcin can be hydrolysed by boiling water, but in absence of another reagent, the p-phenetidine reacts with unchanged Dulcin to give the disubstituted product, di-p-phenetole-carbamide, [16].

In the production of ammonia from urea the reaction becomes rapid at around 130 °C, [17].



**Figure 2** From Dulcin to the quinonoid salt

The hydrolysis to p-phenetidine in these colour tests is confirmed since the reaction mixture is heated in a boiling water bath for 5-10 minutes. Once phenetidine is formed, the molecule loses 2 electrons in one electron steps, that is, at nitrogen (amine) and at oxygen (phenyl ether). These radical cations can have resonance to cations derived from p-quinone mono-imine, which form nitrate or chloride salts. These compounds are related to blue violet Wurster's salts, [18]. The inorganic reagents are reduced to  $\text{Ag}^0$  in the case of silver nitrate, or to  $\text{Hg}^{+1}$  when mercuric nitrate, or mercuric chloride, is used. This reaction route, Figure 2, is in accordance with the chemical department of the involved substances, with the experimental conditions, and explains the violet colour observed in these assays for Dulcin.

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#### 4 Conclusion

The chemistry of Dulcin detection by means of electron transfer reactions has been disclosed. The tests which employ mercury nitrate (Jorissen), and silver nitrate or mercury chloride (Ruggeri) have been cleared up. The first reaction is the hydrolysis of the ureido chain in Dulcin. The reaction mechanism of this step is different from amide hydrolysis. Isomerization to imidol favours formation of a dipolar ion suitable for C-N fission. 1,4-Phenetidine and isocyanic acid are formed. The latter is hydrated across the C=N double bond, yielding a carboxyl group which is prone to produce a zwitterion that affords carbon dioxide and ammonia.

The phenetidine molecule can donate electrons to the cations used in the tests, which can be reduced by electron transfer. This way, compounds similar to Wurster's salts are obtained, explaining the formation of violet colour in these tests.

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#### Compliance with ethical standards

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##### *Disclosure of conflict of interest*

There is no conflict of interest to declare.

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