ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 4, 1985

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# OXIDATION OF CINNAMALDEHYDE AND CINNAMIC ACID WITH CERIUM (IV) IN PERCHLORIC ACID SOLUTION

The effect of various reagents on the rate of cerium (IV) reduction with cinnamaldehyde and cinnamic acid was studied by way of potentiometric determination of the unreacted oxidizer in samples of the reaction mixtures. It was found that the stable intermediate product arising in the course of oxidation of the two compounds is benzoic aldehyde.

The literature data concerning the reaction of cinnamaldehyde and cinnamic acid with various oxidizers indicate that the mechanisms involved depend on the kind of oxidizer used. Cinnamaldehyde oxidized by selenium dioxide [1] yields hydroxycinnamic acid as the end product. According to some authors [2] the rate of cinnamic acid oxidation by osmium tetraoxide depends on the clevage of complex bonds, with enol being the end product. This acid has also been oxidized by potassium permanganate [3-5]. In a perchloric acid medium, the reaction rate is limited by the process of hypomanganate ester oxidation to benzaldehyde and glyoxalic acid. When the oxidation of cinnamaldehyde and cinnamic acid was effected by the use of cerium perchlorate, one should expect the first stage of the process to be an attack of the oxidizer on the double bond. Previous research has shown that oxidation of the aldehyde group to the carboxyl group is hard to carry out. In the process involving aromatic aldehydes, the rate of aldehyde group oxidation is comparable to the rate of aromatic ring clevage.

## Experimental

### Measurement procedure

The stoichiometry and rate of cinnamaldehyde and cinnamic acid oxidation by cerium perchlorate were determined at 60°C. Oxidizer concentration in the reaction mixture was established by potentiometric determination of unreacted cerium (IV) using sodium oxalate, samples for these determinations were taken at predetermined time intervals.

The absorbance of the post-reaction mixtures with different oxidizer - reducer molar ratios was measured by means of a SPECORD UV VIS (Carl Zeiss Jena) spectrophotometer at 200-350 nm, using 1 cm quartz cuvettes.

### Reagents and solutions

Cerium perchlorate 1.2 mole/l in a 6 mole/l solution of perchloric acid was prepared according to Smith and Getz [6]. Its molarity was determined amperometrically using titrated sodium oxalate solution [7].

Sodium oxalate - 0.05 mole/l solution.

Perchloric acid - 9.8 mole/l solution.

Cinnamaldehyde - p. a.

Cinnamic acid - p. a.

Since neither compound dissolves well in water, separate samples were prepared for each kinetic measurement. Prior to the investigation, cinnamaldehyde had been distilled under reduced pressure, collecting the fraction of the appropriate boiling temperature. Cinnamic acid was crystallized from hot water. The concentration of the solutions for spectrophotometric investigations was 0.001 mole/l.

### Results and discussion

In order to determine the stoichiometry of the processes under study, samples containing 0.5 mmole of the approriate reducing agents were oxidized in a 2 mole/l perchloric acid solution using 100 - fold molar excess of the oxidizer. It was found, that complete oxidation of 1 mole of both cinnamaldehyde and cinnamic acid requires ca. 36 mmole of cerium (IV). The post-reaction mixtures were found to contain carbon dioxide and formic acid. However, the time required for complete oxidation of both components to take place is very long and equals several dozen days. In such a case, the results obtained depend in large measure on the very slow process of cerium (IV) reduction by water [8] as well as oxidation of formic acid by cerium (IV) a process that takes several months. It is, however difficult to establish the exact amount of formic acid that has become oxidized to $CO_2$ and by the same token, to write a general equation of the oxidation of cinnamaldehyde and cinnamic acid by cerium (IV).

The rate of the oxidation reaction was investigated at different initial concentrations of the reagents in a 2 mole/l perchloric acid solution. The results obtained are presented in Fig. 1.

It can be seen in Fig. 1 that a two-fold increase of the initial concentration of both reductors in the reacting mixture brings about a two-fold increase of the reaction rate, while a twofold increase of cerium (IV) concentration has practically no effect on the rate of oxidation of the compounds under investigation. This suggests that in the range of concentrations studied the processes involved are of the first order relative to the reducers and zero order relative to the oxidizer. The dependences of Fig. 1 also show a marked lowering of the reaction rate if the reduced amounts of cerium (IV) corresponds to higher than ca. eight-electron transformations. This suggests that oxidation of cinnamaldehyde and cinnamic acid with cerium (IV) involves sequential reactions of substantially different rates, a suggestion that is supported by measurements of the reduction times of successive cerium (IV) portions added to the reducers under study in amounts corresponding to one-electron transformations (Fig. 2).

A distinct lengthening of the reduction time occurs in both cases during the reduction of the ninth portion of the oxidizer, indicating the formation of stable intermediate products in

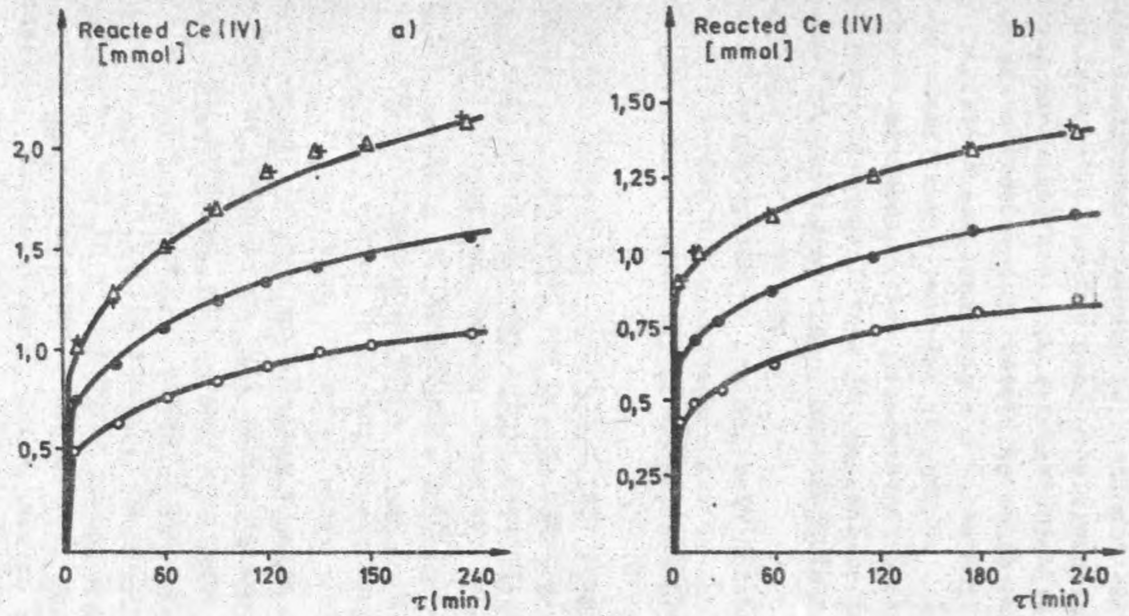


Fig. 1. Effect of regent concentration on the rate of cerium (IV) reduction by: a) cinnamaldehyde (al) and b) cinnamic acid (ac) in reaction mixture of composition

$Ce^{4+}$ - 5 · $10^{-2}$ mole/l; ○al = ○ac = 5 · $10^{-4}$ mole/l

$Ce^{4+}$ - 5 · $10^{-2}$ mole/l; ●al = ●ac = 7·5 · $10^{-4}$ mole/l

$Ce^{+4}$ - 5 · $10^{-2}$ mole/l +al = +ac = 1 · $10^{-3}$ mole/l

$Ce^{+4}$ -10 · $10^{-2}$ mole/l Δal = Δac = 1· $10^{-3}$ mole/l

in a 2 mole/l $HClO_4$ medium at 60°C

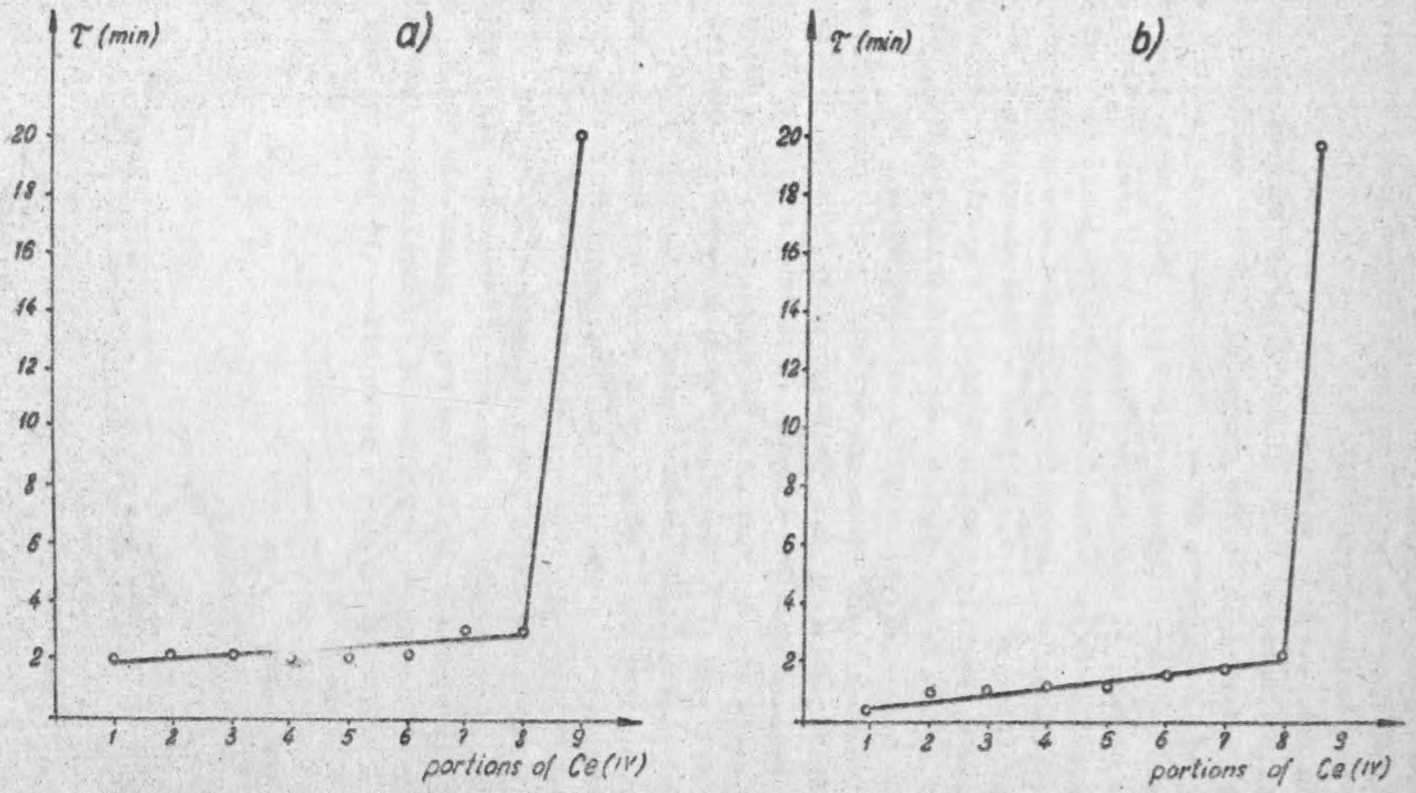
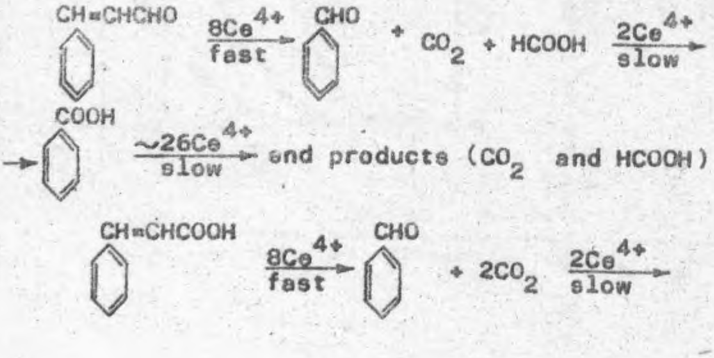


Fig. 2. Reduction times of the successive portions of cerium (IV) added to compounds under study in amounts corresponding to one-electron transformations. a) cinnamaldehyde, b) cinnamic acid

eight-electron transformations. In view of this we measured the 200-350 nm spectra of the post-reactions mixtured with different oxidizer-reducer molar ratios (Fig. 3).

In the initial stage of cinnamaldehyde oxidation (Fig. 3a) there is a slight decay of its characteristic absorbance spectra which is proportional to the amount of reduced cerium (IV). The lovering of the spectra is not accompanied by a shift of their maxima towards shorter wavelenghts, which means that the intermediate product of cinnamaldehyde is not cinnamic acid. As the oxidzer-reducer molar ratio increases there begin to appear new bands characteristic of compounds containing aldehyde groups. For the molar ratio of 1 : 8, well-developed absorbance bands characteristic of benzoic aldehyde appear. A similar situation was observed in the course of cinnamic acid oxidation (Fig. 3b). A small molar excess of the oxidizer is accompanied by gradual decay of the absorbance bands characteristic of cinnamic acid. As the oxidizer-reducer molar ratio increases, bands characteristic of benzoic aldehyde appear. It follows from Fig. 3b that the highest yield of its formation corresponds to molar ratio of 1 : 8. For the sake of comparison, we measured the 200-350 nm spectrum for benzoic aldehyde whose concentration was equal to the initial concentration of cinnamic acid. The absorbance bands obtained different from those for the post-reaction 1 : 8 cinnamic acid-cerium (IV) mixture only slightly and only with respect to the height. This is probably due to partial oxidation of the forming aldehyde to acid, with the rates of benzoic acid formation and of its subsequent oxidation being comparable [9].

Considering the above, oxidation of cinnamaldehyde and cinnamic acid with cerium (IV) in a perchloric acid medium can be written as follows:



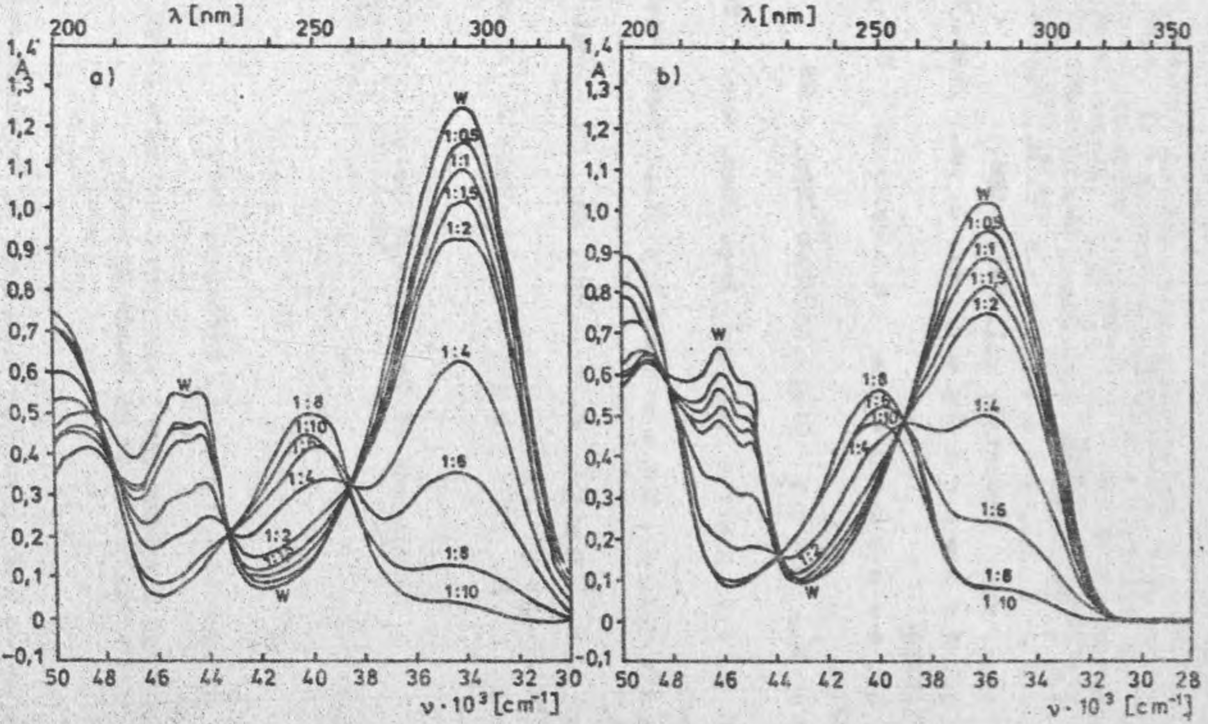
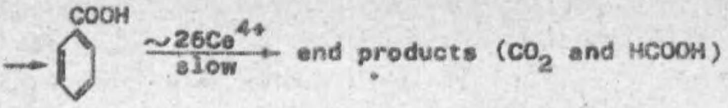


Fig. 3. Absorption spectra for samples of post-reaction mixtures of different oxidizer-reducer molar ratios. a) cinnamaldehyde, b) cinnamic acid, wz - initial spectra of reducers



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## UTLENIANIE ALDEHYDU CYNAMONOWEGO I KWASU CYNAMONOWEGO CEREM (IV) W ROZTWORZE KWASU NADCHLOROWEGO

Określono wpływ poszczególnych reagentów na szybkość redukcji ceru (IV) przez aldehyd cynamonowy i kwas cynamonowy drogą potencjometrycznego oznaczania nieprzereagowanego utleniacza w próbkach mieszanin reagujących. Wykazano, że trwałym produktem pośrednim powstającym podczas utleniania obu związków jest aldehyd benzoesowy.

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## ОКИСЛЕНИЕ КОРИЧНОГО АЛЬДЕГИДА И КОРИЧНОЙ КИСЛОТЫ ЦЕРИЕМ (IV) В РАСТВОРЕ ХЛОРНОЙ КИСЛОТЫ

Определено влияние отдельных реагентов на скорость восстановления церия (IV) коричным альдегидом и коричной кислотой путем потенциометрического определения концентрации окислителя в пробах реагирующих смесей. Показано, что стабильным промежуточным продуктом образующимся в течение реакции окисления этих соединении является бензальдегид.