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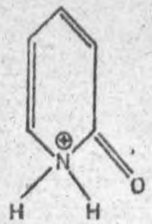
STUDIES ON THE OXIDATION OF HYDROXYPYRIDINES WITH CERIUM PERCHLORATE IN PERCHLORIC ACID MEDIUM

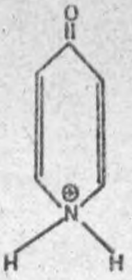
The effect of the concentration of various reagents on the rate of hydroxypyridines oxidation with cerium (IV) in aqueous solutions of perchloric acid was studied by way of amperometric determination of cerium ions concentration in samples of the reacting mixtures using titrated solution of sodium oxalate. The stoichiometry of the reactions was determined and it was found that they proceed in several stages. In the case of 2-hydroxypyridine oxidation an intermediate product was isolated and it was shown that the reaction rate is limited by the decomposition rate of the complex substrate with cerium ions and by the decomposition rate of the complex with the intermediate product. On this basis the kinetic parameters of these processes were calculated.

The present investigation is part of a series of studies on the oxidation of aromatic compounds by cerium perchlorate [1-4]. The pyridine ring is basically resistant to oxidation and, as a rule, the reaction yields appropriate N-oxides [5-8]. On the other hand, when persulfates [9, 10], Fenton's reagent [11], or oxygen in statu nascendi [12] are used, a cleavage of the pyridine ring takes place. This has also been observed in the course of anode oxidation on nickel [13]. The authors of the above-mentioned papers report a number of intermediate products, with the reaction mechanism involved being similar. In order to establish the stoichiometry of the reaction and to determine its kinetic parameters, oxidation of pyridine derivatives was carried out using cerium perchlorate as the oxidizer [14-17] in a perchloric acid solution. Considering the reaction medium employed $[H^+] \geqslant 1$ mole/dm^3 one can assume that the oxidized compounds occur mainly as protonized forms [18]:



of pyridine-2

3-hydroxypyridine



pyridine-4

Experimental

Reagents and solutions

0.1 and 0.85 mole/dm^3 solutions of cerium perchlorate in 2.0 mole/dm^3 perchloric acid solution were prepared in accordance with Smith and Getz [15]. The titer of the solution was determined by the amperometric method using 0.05 mole/dm^3 sodium oxalate solution [19, 20]. Perchloric acid determinations in cerium perchlorate solution were made alkacimetrically after cerium (IV) had been reduced with sodium oxalate solution [21] The sodium oxalate solution employed in cerium (IV) determinations was prepared from weighed samples.

The perchloric acid used (p.p.a), whose concentration was 10.62 mole/dm^3, was manufactured by VEB-LABOR-Chemie Apolda. Preparations of 2-, 3- and 4-hydroxypyridine (Ioba Chem.) were purified by repeated crystallization from water-ethanol mixture (70 wt %).

The melting temperatures of these compounds after crystallization and drying at 328 K under reduced pressure were:

2-hydroxypyridine - 378.5 - 379.5 K,

3-hydroxypyridine - 401-402 K,

4-hydroxypyridine - 419.5-420.5 K.

The ground solutions of these compounds (0.1 and 0.01 mole/dm^3) were obtained by dissolving appropriate weighed samples in a laboratory flask. All solutions were prepared using water triply distilled under laboratory conditions.

Procedure employed

The stoichiometry of the oxidation of the above compounds with cerium perchlorate was established in two ways.

1. Samples of the reducing agents containing 2×10^{-5}, 5×10^{-4} and 10^{-4} mole of the compounds studied were poured into laboratory flasks, acidified with perchloric acid in an amount that yielded its concentration of 1 mole/dm^3, and a predetermined amount of cerium perchlorate was added; cerium perchlorate was in excess relative to the reducing agent, and the overall volume of the mixture was 0.1 dm^3. The reaction was carried out at 340 K. Samples of the reaction mixture were taken every 30 min and cerium (IV) concentration in them was determined amperometrically using titrated solution of sodium oxalate [19, 20]. After ca. 5 hrs the concentration practically stopped changing.

2. 2 mmole portions of 0. 85 mole/dm^3 cerium perchlorate were added to a solution containing 1 mmole of the compound under investigation and 1 mole/dm^3 of perchloric acid. The temperature of the solutions was 343 K. Each successive portion of cerium perchlorate was added after the previous one had been reacted. The time required for a given portion to be reduced was recorded. In order to determine the dependence of the reaction rate on the concentration of the different reagents, solutions were prepared in laboratory flasks containing appropriate amounts of cerium perchlorate, perchloric acid and water. The amount of water was selected in such a way that the volume of the mixture, together with the reducing agent, was 0.1 dm^3. Following thermostating at 323 K, an appropriate amount of the reducing agent was added. From the reaction mixture samples of 0.01 dm^3 were taken at suitable time intervals and cerium (IV) concentration was determined amperometrically using titrated sodium oxalate solution.

Results and conclusions

The results of stoichiometry investigation (Tab. 1, 2) indicate that oxidation of pyridine-2, pyridine-4 and 3-hydroxypyridine with cerium perchlorate is connected with 18-electron transformations.

Table 1

Determination of the stoichiometry of hydroxypyridine oxidation with cerium perchlorate. Five determinations were made for each amount of oxidized compound

Compound	Number of mmol	Molar oxidizer--reducer concentration ratio	Molar ratio of the amount of oxidized Ce^{+4} to the amount of the reducer
pyridon-2	0.2	60 : 1	18.03 : 1
	0.5	50 : 1	17.97 : 1
	1.0	40 : 1	17.96 : 1
3-hydroxy-pyridine	0.02	60 : 1	18.02 : 1
	0.05	50 : 1	18.09 : 1
	0.10	40 : 1	17.98 : 1
pyridon-4	0.02	60 : 1	17.86 : 1
	0.05	50 : 1	17.96 : 1
	0.10	40 : 1	17.92 : 1

Table 2

Reduction time of the given portion of cerium perchlorate

Sample number	Number of mmoles of ceric chloride added at one time	Pyridon-2	3-hydroxy-pyridine	Pyridon-4
1	2	3	4	5
1	2	immediately	immediately	3 min
2	2	immediately	immediately	6 min
3	2	immediately	immediately	13 min
4	2	1 min	0.10 min	23 min
5	2	4 min	0.33 min	37 min
6	2	17 min	1 min	50 min
7	2	36 min	1 min	100 min
8	2	92 min	2 min	220 min

Table 2 (cont.)

1	2	3	4	5
9	2	210 min	5 min	ca. 360 min
10	2	Ce^{+4} concentration practically does not change	Ce^{+4} concentration practically does not change	Ce^{+4} concentration practically does not change

The end products of these processes were found to be CO_2, HCOOH and NH_4^+. Under the experimental conditions, the formic acid that arises does not become oxidized by cerium ions [21, 22].

Considering the above data, oxidation of the compounds under study with cerium perchlorate can be written as follows:

$$C_5H_6NO^+ + 18Ce^{+4} + 9H_2O \longrightarrow 4CO_2 + HCOOH + NH_4^+ + 18H^+ + 18Ce^{+3}$$

The results of kinetic investigations are presented in Figs. 1-3.

The percentages of the reacted cerium (IV) required for the oxidation of a given amount of the reducing agent are indicated on the ordinate. Plots 1c, 2c and 3c depict the time dependence of the degree of oxidation for mixtures in which the initial cerium perchlorate concentration was equale to the product of the electronicity of the process and reducer concentration. The plots obtained show that a two-fold increase of the reducer concentration gives rise to an almost two-fold increase of the reaction rate. Thus, for example, during 60 min of 3-hydroxypyridine oxidation 0.69×10^{-3} mole Ce (IV) became reduced, where the initial concentrations of 3-hydroxypyridine and cerium perchlorate were 4.444×10^{-4} and 4×10^{-1} mole/dm^3 respectively. On the other hand, for initial concentrations of 8.889×10^{-4} and 4×10^{-2} mole/dm^3 respectively, the amount of Ce (IV) that became reduced was 1.39×10^{-3} mole. It follows that an increase in the cerium perchlorate concentration has practically no effect on the reaction rate.

Nor does the reaction rate depend on the perchloric acid concentration: an increase in its concentration from 1 to 4 mole/dm^3 accelerates the process by only ca. 5 per cent, and that acceleration can be attributed to increased ionic strength.

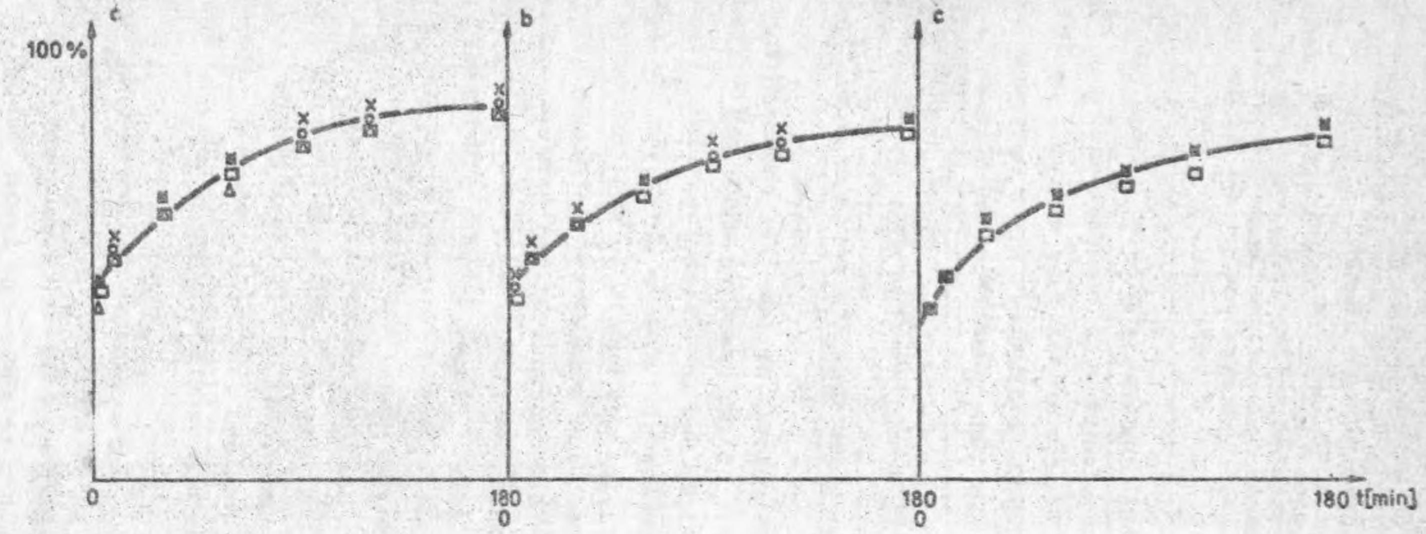


Fig. 1. Degree of cerium perchlorate oxidation - pyridon-2. Initial concentration (mole/dm^3)

a

Ce (IV)	Pyridon-2
x $4 \cdot 10^{-2}$	$4.444 \cdot 10^{-4}$
o $4 \cdot 10^{-2}$	$8.889 \cdot 10^{-4}$
□ $4 \cdot 10^{-2}$	$1.333 \cdot 10^{-3}$
△ $8 \cdot 10^{-2}$	$8.889 \cdot 10^{-4}$

b

Ce (IV) - $8 \cdot 10^{-2}$

Pyridon-2
x $8.889 \cdot 10^{-3}$
o $1.778 \cdot 10^{-3}$
□ $2.667 \cdot 10^{-3}$

c

Ce (IV)	Pyridon-2
x $2 \cdot 10^{-2}$	$1.111 \cdot 10^{-3}$
o $4 \cdot 10^{-2}$	$2.222 \cdot 10^{-3}$
□ $8 \cdot 10^{-2}$	$4.444 \cdot 10^{-3}$

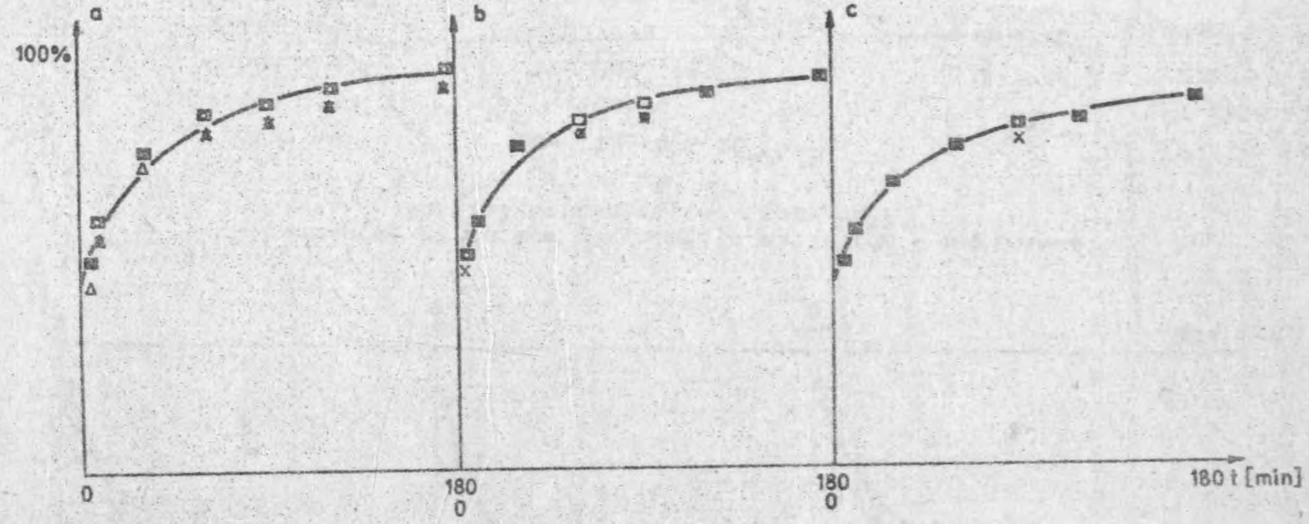


Fig. 2. Degree of cerium perchlorate oxidation - 3-hydroxypyridine.
Initial concentration (mole/dm^3)

a

Ce (IV)	3-hydroxypyridine
× 4 . 10^{-2}	4.444 . 10^{-4}
o 4 . 10^{-2}	8.889 . 10^{-4}
□ 4 . 10^{-2}	1.333 . 10^{-3}
Δ 8 . 10^{-2}	8.889 . 10^{-4}

b

Ce (IV) 8 . 10^{-2}

3-hydroxypyridine
× 8.889 . 10^{-3}
o 1.7778 10^{-3}
□ 2.667 . 10^{-3}

c

Ce (IV)	Pyridon-2
× 2 . 10^{-2}	1.111 . 10^{-3}
o 4 . 10^{-2}	2.222 . 10^{-3}
□ 8 . 10^{-2}	4.444 . 10^{-3}

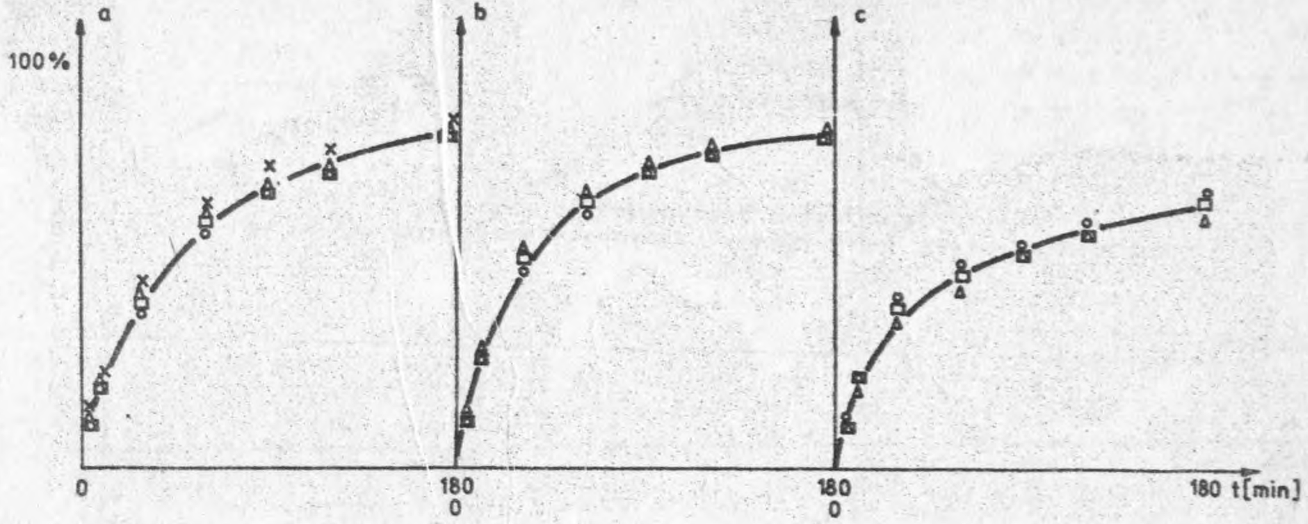


Fig. 3. Degree of cerium perchlorate oxidation - pyridon-4. Initial concentration (mole/dm^3)

a

Ce (IV)	Pyridon-4
Δ 4 . 10^{-2}	4.444 . 10^{-4}
□ 4 . 10^{-2}	8.889 . 10^{-4}
o 4 . 10^{-2}	1.333 . 10^{-3}
x 8 . 10^{-2}	8.889 . 10^{-4}

b

Ce (IV) 8 . 10^{-2}

Pyridon-4
Δ 8.889 . 10^{-4}
□ 1.7778 . 10^{-4}
o 2.667 . 10^{-4}

c

Ce (IV)	Pyridon-4
Δ 2. 10^{-4}	1.111 . 10^{-3}
□ 4 . 10^{-4}	2.222 . 10^{-3}
o 8 . 10^{-4}	4.444 . 10^{-3}

The kinetics of the oxidation of the compounds under study are complex, because in the course of the first 10 min of the process about 60 per cent of the required cerium (IV) became reduced in the reaction with 3-hydroxypyridine, about 50 per cent - in the reaction with pyridone-2, and between 25 and 30 per cent - in the reaction with pyridone-4, while during the next 10 min only 10 per cent of cerium (IV) undergo reduction.

We were unable to determine the effect of the oxidizer and reducer concentration on the reaction rate under conditions of

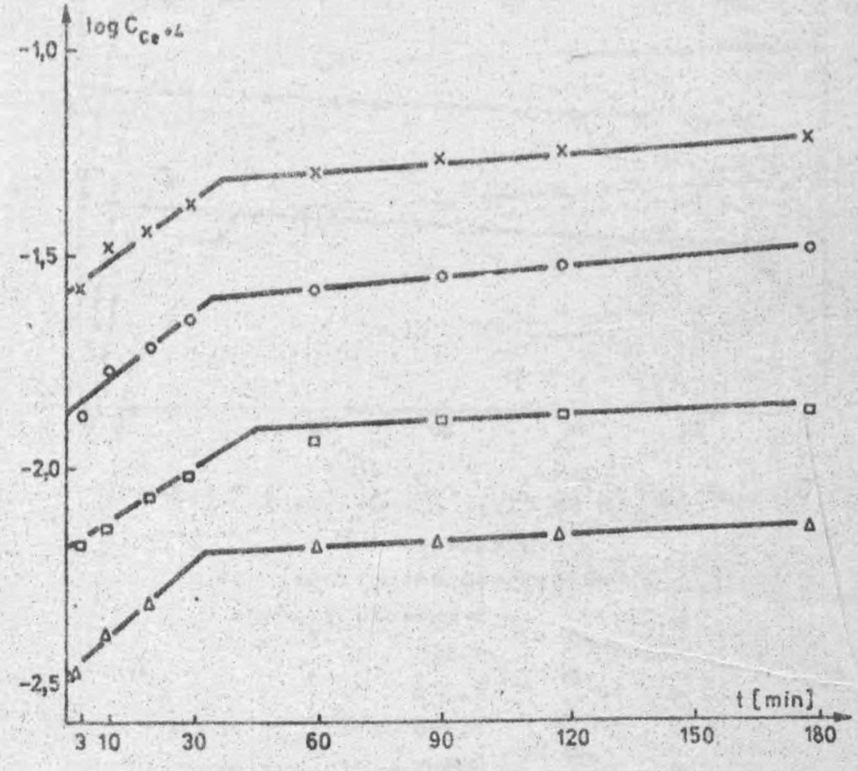


Fig. 4. Plot of $\lg\left(C_{0\ Ce(IV)} - C_{t\ Ce\ (IV)}\right) = f\ (t)$ - pyridon-2.

Initial concentration (mole/dm^3)

	Ce (IV)	Pyridon-2
×	$8 \cdot 10^{-2}$	$8.889 \cdot 10^{-3}$
o	$4 \cdot 10^{-2}$	$2.222 \cdot 10^{-3}$
□	$8 \cdot 10^{-2}$	$1.778 \cdot 10^{-4}$
Δ	$4 \cdot 10^{-2}$	$8.889 \cdot 10^{-4}$

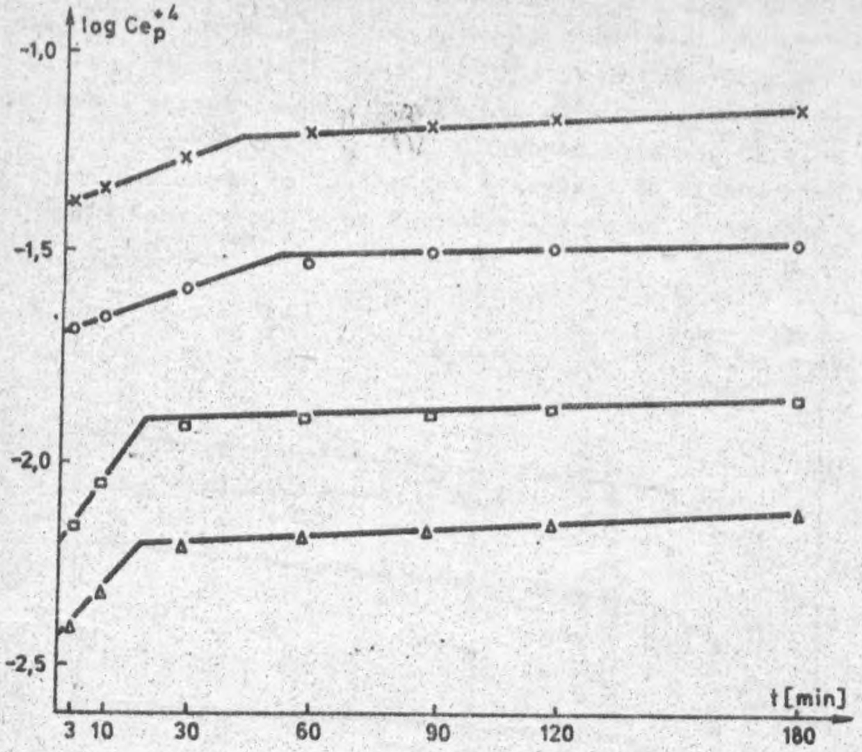


Fig. 5. Plot of $\lg\left(C_{0\ Ce\ (IV)} - C_{t\ Ce\ (IV)}\right) = f(t)$ - 3-hydroxypyridine.

Initial concentrations

	Ce(IV)	3-hydroxypyridine
×	$8 \cdot 10^{-2}$	$8.889 \cdot 10^{-3}$
o	$4 \cdot 10^{-2}$	$2.222 \cdot 10^{-3}$
□	$8 \cdot 10^{-2}$	$1.778 \cdot 10^{-4}$
Δ	$4 \cdot 10^{-2}$	$8.889 \cdot 10^{-4}$

oxidizer insufficiency because 60-80 per cent of cerium perchlorate undergo oxidation almost immediately (even at 273 K).

It follows from the dependences of the logarithm of cerium (IV) concentration on time (Figs. 4-6) that the processes of pyridone-2 and 3-hydroxypyridine oxidation proceed in two stages, while pyridone-4 oxidation is probably a three-stage process.

We succeeded in determining the electronicity of the different stages of the process for pyridone-2 and 3-hydroxypyridine.

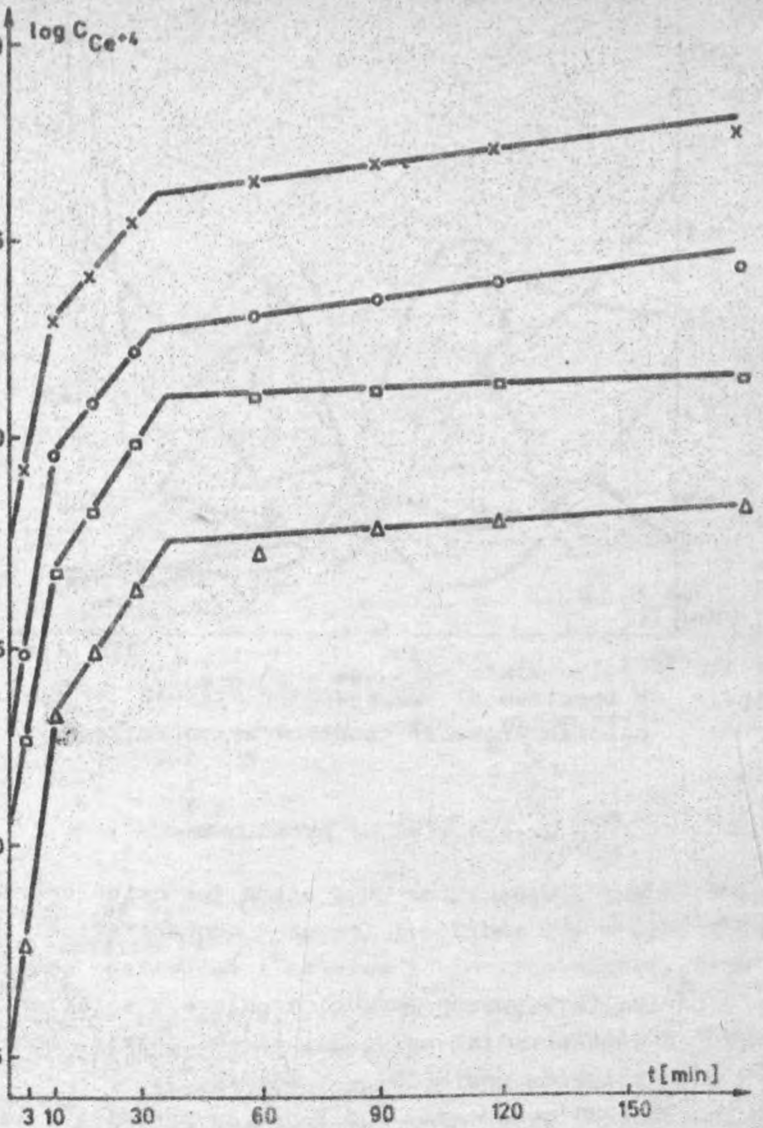


Fig. 6. Plot of $\lg(C_{U\,Ce(IV)} - C_{t\,Ce(IV)}) = f(t)$ - pyridon-4.

Initial concentrations

	Ce(IV)	Pyridon-4
x	$8 \cdot 10^{-2}$	$8.889 \cdot 10^{-3}$
o	$4 \cdot 10^{-2}$	$2.222 \cdot 10^{-3}$
□	$8 \cdot 10^{-2}$	$1.778 \cdot 10^{-4}$
Δ	$4 \cdot 10^{-2}$	$8.889 \cdot 10^{-4}$

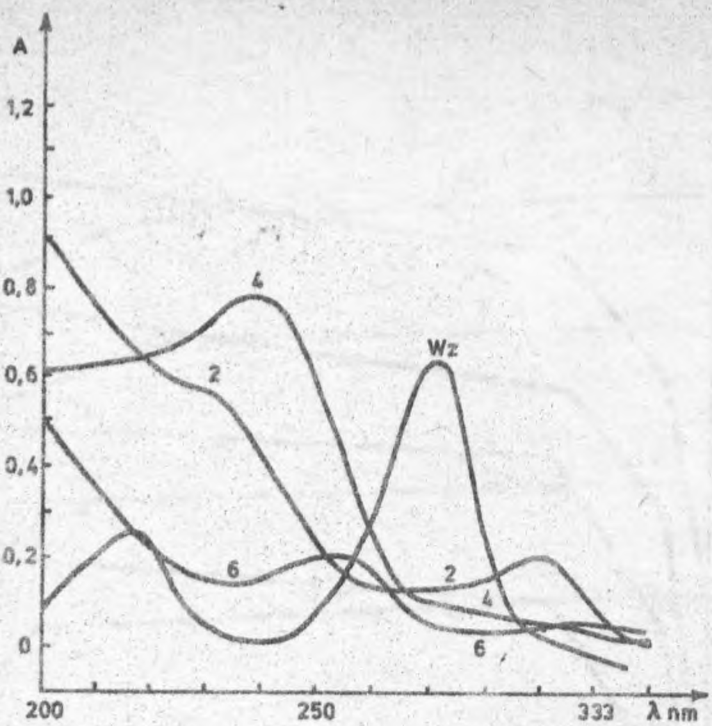


Fig. 7. UV spectrum of the reaction mixture for pyridon-2
Oxidizer-reducer concentration ratio
2 2 : 1
4 4 : 1
6 6 : 1
Wz-spectrum of pyridon-2

Figures 7, 8 and 9 depict the UV spectra for oxidizer-reducer ratios of 2 : 1, 4 : 1 and 6 : 1 (reducer concentration 10^{-4} mole/ /dm^3, $HClO_4$ concentration - 1 mole/dm^3) following complete reduction of cerium (IV), using cerous perchlorate solution as reference (whose concentration was equal to the initial concentration of cerium perchlorate and $HClO_4$ - 1 mole/dm^3).

In the case of pyridone-2 and 3-hydroxypyridine oxidation, an increase of the oxidizer-reducer concentration ratio is accompanied by decay of the 270 nm absorption band, while the local maximum at 220 nm shifts towards longer wavelengths to disappear almost completely for the 6 : 1 ratio. In the case of pyridone-4 oxidation, on the other hand, probably because of the relatively small differences in the rates of the different stages, it is impossible to unequivocally determine the electronicity of the

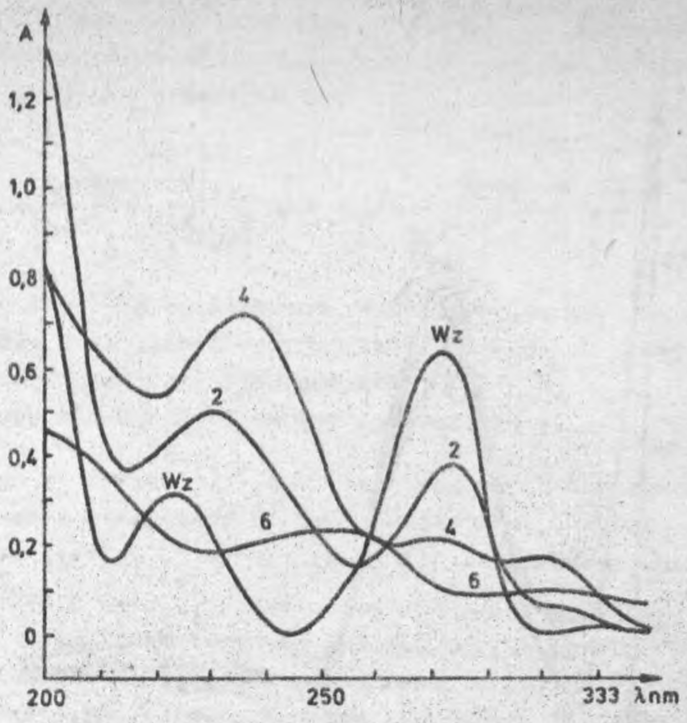


Fig. 8. UV spectrum of the reaction mixture for 3-hydroxypyridine

Oxidizer-reductor	concentration ratio
2	2 : 1
4	4 : 1
6	6 : 1

Wz-spectrum of 3-hydroxypyridine

reaction stages since regardless of the oxidizer-reducer ratio the post-reaction mixture will contain pyridone-2 and intermediate products.

In view of the above, and considering the fact that following mixing of pyridone-2 or 3-hydroxypyridine solutions there appears a deepening of cerium perchlorate colour which recedes after some time, the oxidation mechanism of these compounds may be represented as:

$$C_5H_6NO + Ce^{+4} \rightleftharpoons \text{complex}$$

$$\text{complex} + 5\ Ce^{+4} \xrightarrow{\text{rapidly}} A + 6\ Ce^{+3}$$

$$A + 12\ Ce^{+4} \xrightarrow{\text{slowly}} \text{end products} + 12\ Ce^{+3}$$

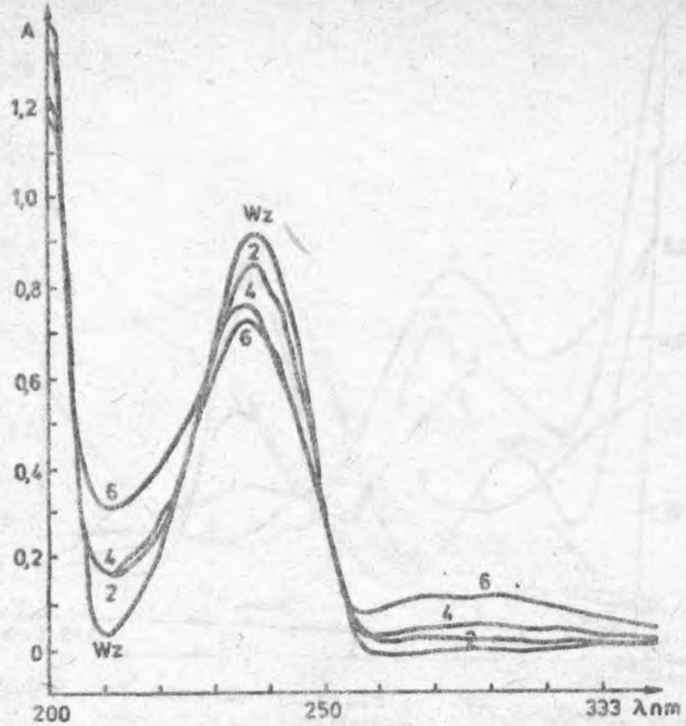


Fig. 9. UV spectrum of the reaction mixture for pyridon-4

Oxidizer-reductor	concentration ratio
2	2 : 1
4	4 : 1
6	6 : 1

Wz - spectrum of pyridon-4

Basing of the results obtained, and adopting the assumption - often made in the literature [1, 4, 23, 24] that oxidation of organic compounds by cerium ions involves formation of complexes before transfer of unpaired electrons, one can say that these processes are limited by the concentration of pyridone-2 and 3-hydroxypyridine complexes with cerium ions, the concentration of the intermediate products (which arise in six-electron transformations) with cerium ions, as well as the rate of electron transfer inside the complexes. For that reason the kinetic equation of the oxidation of these compounds can be represented as:

$$- \frac{d_{C_{Ce^{+4}}}}{dt} = 6 \times K_1 \times [\text{complex I}] + 12 \times K_2 \times [\text{complex II}] \qquad (1)$$

where K_1 and K_2 are rate constants of electron transfer inside the first and second complex respectively, and the concentrations of the complexes are described by:

$$\beta_1 = \frac{[\text{complex I}]}{\left[Ce^{+4}\right] \times \left[C_{red}\right]} \text{ and } \beta_2 = \frac{[\text{complex II}]}{\left[Ce^{+4}\right] \times \left[C_A\right]}$$

Assuming that the equilibrium of the process of complex formation becomes established very quickly, a computer analysis was carried out using an Odra-1305 computer.

The values of $-d_{C_{Ce^{+4}}}$ (dt for appropriate t) at which the concentration of cerium (IV) was measured while the reaction was in progress were determined by differentiating the function $C_{Ce_t^{+4}} = \exp\left[(at^2 + bt + c) : (gt + 1)\right]$ over time. The coefficients a, b and g were obtained using the least squares method, while c was calculated from the initial cerium perchlorate concentration. For nine series of measurements performed for each of the compounds under investigation (different initial oxidizer and reducer concentrations) the most likely values of the stability constants for the complexes as well as the rate constants of electron transfer inside them were obtained by tabulating relation (1) (the values selected were those which exhibited the least deviation from the experimental points). They are: for pyridone-2 - $\beta_1 = 0.018$ dm^3/mole, $K_1 = 0.025$ sec^{-1}, $\beta_2 = 0.009$ dm^3/mole, $K_2 = 0.008$ sec^{-1}, for hydroxypyridine -$\beta_1 = 0.023$ dm^3/mole, $K_1 = 0.036$ sec^{-1}, $\beta_2 = 0.017$ dm^3/mole, $K_2 = 0.007$ sec^{-1}, with the error involved in their determination being estimated at ± 25%.

In the case of pyridone-2 oxidation, the mechanism assumed was confirmed by the isolation of intermediate products (obtained in a six-electron transformation). These products were isolated in the following way: the post-reaction mixture (initial Ce (IV) pyridone-2 concentration ratio of 6:1) was neutralized by means of $KHCO_3$. Then, following removal of the sediment ($KClO_4$ and $Ce(OH)_3$, water was evaporated under reduced pressure. It turned out that in the final stage of water evaporation (temperature ~330 K, pressure ~20 hP) maleic acid imide sublimation sets in, and formic acid distils off. After these compounds had been removed, the mixture contained maleic acid, ammonium maleate, and a small quantity of unidentified compounds.

If in the final stage of neutralization NH_4HCO_3 was used instead of $KHCO_3$, and if sublimation is carried out at a higher temperature (ca. 350 K), then after sublimation of amide no maleic acid or any of its derivatives was found in the mixture. The yield of the imide obtained in this way (relative to pyridone-2) was ca. 50%.

The results presented above permit the conclusion that the intermediate product (A) of the oxidation of pyridone-2 with cerium perchlorate is one of the following there compounds: maleic acid (ammonium ion is also formed), maleic acid amide or imide (the least two compounds arise in protonized form). The first stage of the process can thus be presented in the following form:

$$\text{complex I} + 5Ce^{+4} \longrightarrow A + HCOOH + 6Ce^{+3}$$

The present study was carried out as part of project MR I-11.

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BADANIA NAD REAKCJAMI UTLENIANIA HYDROKSYPIRYDYN NADCHLORANEM CEROWYM W ŚRODOWISKU KWASU NADCHLOROWEGO

Określono wpływ stężeń poszczególnych reagentów na szybkość reakcji utleniania hydroksypirydyn cerem (IV) w wodnych roztworach kwasu nadchlorowego drogą amperometrycznego oznaczania stężenia jonów cerowych w próbkach mieszanin reagujących za pomocą mianowanego roztworu szczawianu sodowego.

Wyznaczono stechiometrię reakcji oraz ustalono, że reakcje przebiegają kilkuetapowo. W przypadku utleniania 2-hydroksypirydyny wydzielono produkt pośredni i wykazano, że szybkość rozpadu kompleksu substratu z jonami cerowymi i szybkość rozpadu kompleksu z produktem pośrednim limituje szybkość reakcji. Na tej podstawie wyliczono parametry kinetyczne tych procesów.

Максимилян Игначак, Станислав Комисарский

ИССЛЕДОВАНИЯ РЕАКЦИИ ОКИСЛЕНИЯ ОКСИПИРИДИНОВ ПЕРХЛОРАТОМ ЦЕРИЯ В СРЕДЕ ХЛОРНОЙ КИСЛОТЫ

Исследовано влияние концентрации отдельных реагентов на скорость окисления оксипиридинов ионами церия (IV) в водных растворах хлорной кислоты путем амперометрического определения концентрации ионов церия с помощью титрованных растворов оксалата натрия. Определена стехиометрия реакции, а также установлено, что реакции протекают ступенчательно.

В случае окисления 2-оксипиридина выделен промежуточный продукт и обнаружено, что скорость реакции лимитирована процессом распада комплексов образованных церием (IV) и субстратом а также церием (IV) и промежуточным продуктом. На этой основе рассчитаны кинетические параметры этих процессов.