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KINETICS OF OXIDATION ACRYLIC AMIDE WITH CERIUM (IV) PERCHLORATE

The amperometric method without the applied external potential was used for the measurements of the reaction rate of cerium perchlorate connected with the acrylic amide oxidation process with cerium (IV) in the presence of the perchlorate acid. The influence of temperature of the reaction rate was also investigated.
The oxidation of acrylic acid by means of the cerium ions is not described in literature.

However, the results are known for the study concerning the oxidation of amides by means of other oxidants neglecting more detailed descriptions of the reaction mechanisms [1-3].

The cerium perchlorate as an oxidant with very high potential reacts completely with the acrylic amide for concentrations of 10^{-2} M in 1 M $HClO_4$ during 1.5 h.

In this paper we present the results of investigations connected with the kinetics of the acrylic acid oxidation with cerium (IV) at the presence of the perchlorate acid. On the basis of the obtained results we can also determine the activation energy.

Experimental

Measurement technique and reagents

The kinetic measurements were made by means of the amperometric. The constant platinium microelectrode was the indicator electrode, while the calomel electrode serves as the reference one.

The solution was intensively mixed by means of the magnetic stirrer. The measurements were made in following order.

The indirect method was applied to determine in the samples taken from the reacting mixture the amount of cerium that has not been acted upon. To do this sodium oxalate solution was used. The equivalent point was determined by the amperometric methods [4-6]. The measurements were taken in temperatures 60, 70 and 80°C (± 0.2°C).

The reacting mixture was thermostated by the thermostat UTM. The solution of cerium perchlorate with 0.1 M concentration in perchlorate acid was prepared according the procedure proposed by S m i t h and G e t z [7]. The concentration of cerium perchlorate was determined by titration with 0.1 N solution of sodium oxalate using the above mentioned amperometric method. For investigations the perchlorate acid (p.p.a.) produced by "Analar" was used.

The solutions of the acrylic amide were prepared from weighed portions of this compound (p.p.a.) produced by "BDH Chemicals Ltd. Poole". To prepare all solutions the twice - destillated water was used.

Results and conclusions

1. The determination of stoichiometry of the acrylic amide oxidation reaction by means of the cerium perchlorate. In this case the products of acrylic amide oxidation are as follows: formic acid, carbon dioxide and ammonia.

T a b l e 1

Determination of stoichiometric ratio

No	T [°C]	Times [hours]	Amide $\bar{a} \cdot 10^2$ [mole/dm^3]	$Ce(ClO_4)_4$ $\bar{b} \cdot 10^2$ [mole/dm^3]	Molar ratio $\bar{b} : \bar{a}$	Means results $\bar{b} : \bar{a}$
1	2	3	4	5	6	7
1	60	1.5	0.50	3.99	7.98	
2	60	2.0	0.50	3.95	7.90	7.96
3	60	2.5	0.50	4.00	8.00	

Table 1 (cont.)

1	2	3	4	5	6	7
4	60	1.5	1.00	7.98	7.98	
5	60	2.0	1.00	8.05	8.05	7.99
6	60	2.5	1.00	7.95	7.95	
7	70	1.0	0.50	3.98	7.96	
8	70	1.5	0.50	4.03	8.06	8.04
9	70	2.0	0.50	4.05	8.10	
10	70	1.0	1.00	7.90	7.90	
11	70	1.5	1.00	8.05	8.05	8.02
12	70	2.0	1.00	8.10	8.10	
13	80	1.0	0.50	4.03	8.06	
14	80	1.5	0.50	4.08	8.16	8.09
15	80	2.0	0.50	4.02	8.04	
16	80	1.0	1.00	8.20	8.20	
17	80	1.5	1.00	8.15	8.15	8.17
18	80	2.0	1.00	8.15	8.15	

The results of measurements presented in Tab. 1 show that the reaction of the acrylic amide oxidation with the cerium perchlorate is accompanied by the 8-electronic transition. On this basis the following equation for this reaction can be proposed

$$CH_2 = CH\text{-}CO\text{-}NH_2 + 8Ce^{+4} + 5H_2O \longrightarrow 8Ce^{3+} + 2HCOOH + 7H^+ + CO_2 + NH_4^+$$

2. Kinetics for the acrylic amide oxidation with the cerium perchlorate.

In order to investigate the kinetics of the process mentioned above the method of analysis was applied which is based on the succesive of the oxidation reaction by means of the fast reduction of cerium by sodium oxalate excess introduced in the known amount.

The rest of the sodium oxalate was determined by titration with the cerium perchlorate. To determine the reaction order in relation to the acrylic amide a series of kinetic measurements was made. Table 2 contains the results of these measurements made for various values of the amid concentration, at the excess of the cerium perchlorate.

Table 2

Determination consumpted of cerium (IV) from the time of the start of the reactions (at the constant concentration of $Ce(ClO_4)_4$)

No	$C_A^o \left[\frac{mole}{dm^3}\right] \cdot 10^4$	Times (min)	$\bar{a} \left[\frac{mole}{dm^3}\right] \cdot 10^4$	No	$C_A^o \left[\frac{mole}{dm^3}\right] \cdot 10^4$	Times (min)	$\bar{a} \left[\frac{mole}{dm^3}\right] \cdot 10^4$
1	6.25	2	1.25	11	8.75	2	1.10
2	6.25	4	2.19	12	8.75	4	2.19
3	6.25	6	3.13	13	8.75	6	3.28
4	6.25	8	3.91	14	8.75	8	4.06
5	6.25	10	4.53	15	8.75	10	4.69
6	7.50	2	1.25	16	10.00	2	1.25
7	7.50	4	2.19	17	10.00	4	2.19
8	7.50	6	3.28	18	10.00	6	3.28
9	7.50	8	4.06	19	10.00	8	4.06
10	7.50	10	4.69	20	10.00	10	4.85

$C^o_{Ce^{+4}} = 4.55 \cdot 10^{-2}$ mole/dm^3, $C_{H^+} = 3.45$ mole/dm^3, T = 333 K.

$\bar{a}$ - concentration consumpted of amide.

$C^o_{Ce^{+4}}$ - concentration of $Ce(ClO_4)_4$.

C_A^o - starting concentration of amide.

The obtained results show that the reaction order for the acrylic amide oxidation with the cerium perchlorate with respect to the amide is equal to zero.

To determine the reaction order with respect to the cerium (IV) perchlorate the investigations using considerable high excess of the acrylic amide were made. The results of measurements for various concentrations of the cerium perchlorate are given in Tab. 3 and the corresponding graphs of the dependence $b = f(t)$ are shown in Fig. 2.

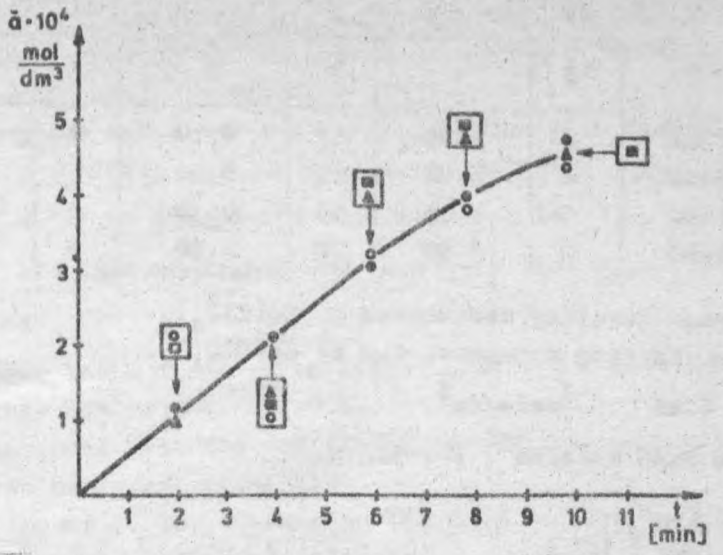

Fig. 1. The dependence of the amount of the reacted amid on the time of the reaction duration for its various initial concentrations

- ● initial concentration of amid - $10 \cdot 10^{-4}$ mole/dm^3
- ▲ initial concentration of amid - $8.75 \cdot 10^{-4}$ mole/dm^3
- ■ initial concentration of amid - $7.50 \cdot 10^{-4}$ mole/dm^3
- ○ initial concentration of amid - $6.25 \cdot 10^{-4}$ mole/dm^3

Table 3

Determination consumpted of cerium (IV) from the time of the start of the reactions (at the variable concentration of $Ce(ClO_4)_4$)

No	C^o_{Ce} $\left[\frac{mole}{dm^3}\right] \cdot 10^3$	Times (min)	$\bar{b}$ $\left[\frac{mole}{dm^3}\right] \cdot 10^3$	No	C^o_{Ce} $\left[\frac{mole}{dm^3}\right] \cdot 10^3$	Times (min)	$\bar{b}$ $\left[\frac{mole}{dm^3}\right] \cdot 10^3$
1	2	3	4	5	6	7	8
1	4.55	2	3.40	11	8.00	2	5.10
2	4.55	3	3.95	12	8.00	3	6.00
3	4.55	4	4.20	13	8.00	4	6.86
4	4.55	-	-	14	8.00	5	7.40
5	4.55	-	-	15	8.00	6	7.65
6	6.80	2	4.60	16	9.10	2	5.02

Table 3 (cont.)

1	2	3	4	5	6	7	8
7	6.80	3	5.60	17	9.10	3	6.20
8	6.80	4	6.02	18	9.10	4	7.08
9	6.80	5	6.35	19	9.10	5	7.70
10	6.80	6	6.60	20	9.10	6	8.35

$\bar{b}$ - mean quantity consumpted of $Ce(ClO_4)_4$.

C^o_{Ce} - starting concentration of $Ce(ClO_4)_4$.

$C^o_A = 6.25 \cdot 10^{-2}$ mole/dm^3.

$C_{H^+} = 3.45$ mole/dm^3, T = 333 K.

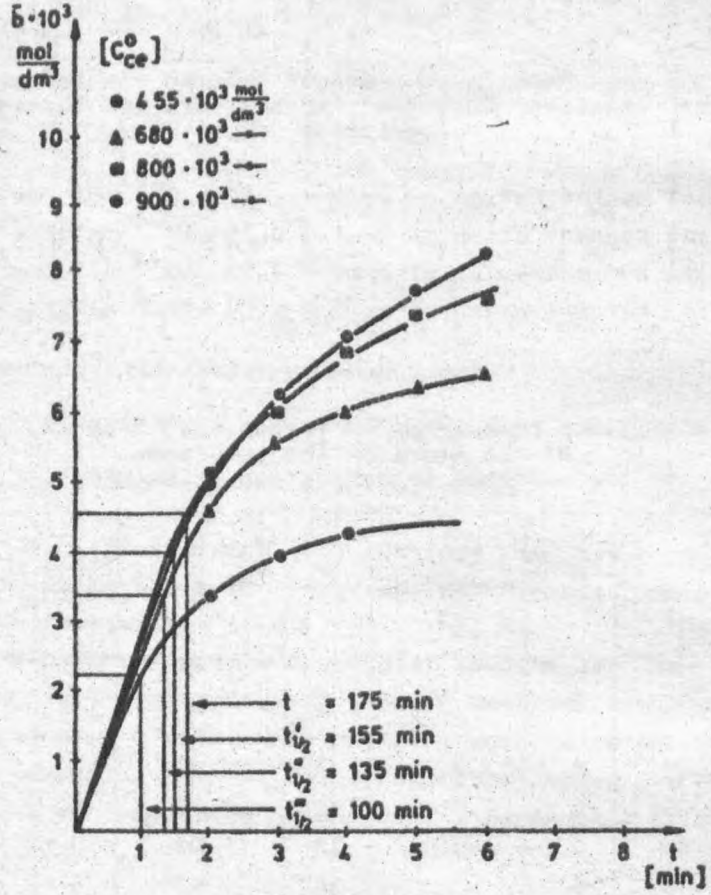

Fig. 2. The curves of the decreasing of the concentration of the cerium perchlorate if the excess of the amid as well as of the perchlorate acid were fixed

The curves illustrating of decreasing the cerium (IV) perchlorate concentration of the excess of the amid as well as of the perchlorate acid are fixed.

Comparing the values of the half-times for the reaction obtained by graph (Fig. 2) and calculated directly from the equation $t_{1/2} = \frac{a}{K_E}$ we obtain the accuracy that is satisfactory. The values K_E are not constants and they vary from $K_E = 6.88$ to $K_E = 3.76$ min.

The above facts allow us to state, that the reaction order varies within the region 0.2-0.6.

This suggests that the reaction is probably proceeds according to two different mechanisms.

3. Influence of temperature on the rate of the acrylic amid oxidation with the cerium perchlorate.

In order to determine the influence of temperature on the reaction rate a series of experiments was made, in which the amid and the cerium perchlorate were used in their stoichiometric amounts. The results are given in Fig. 3.

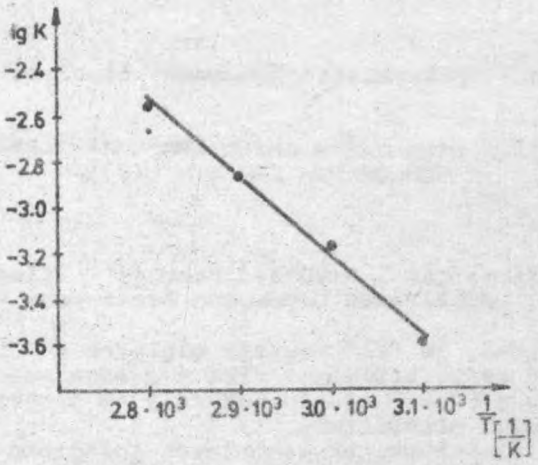

Fig. 3. The function $\lg k = f\left(\frac{1}{T}\right)$

The activation energy was found to be equal to 76.7 kJ/mole.

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KINETYKA UTLENIANIA AMIDU KWASU AKRYLOWEGO NADCHLORANEM CEROWYM (IV)

Zbadano stechiometrię i szybkość reakcji utleniania amidu kwasu akrylowego nadchloranem cerowym w środowisku kwasu nadchlorowego.

W pracy wykazano, że rząd reakcji względem amidu kwasu akrylowego jest równy zeru, natomiast rząd względem nadchloranu cerowego nie jest stały (0.2-0.6), co wskazuje na przebieg reakcji według dwóch różnych mechanizmów.

Na podstawie danych eksperymentalnych obliczono energię aktywacji, która w przedziale temperatur 323-353 K wynosi 18.3 kcal/mol. Zaproponowano również prostą metodę analityczną pozwalającą oznaczyć ilościowo amid kwasu akrylowego.

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КИНЕТИКА ОКИСЛЕНИЯ АМИДА АКРИЛОВОЙ КИСЛОТЫ ПЕРХЛОРАТОМ ЦЕРИЯ(IV)

Исследована стехиометрия и скорость процесса окисления амида акриловой кислоты перхлоратом церия (IV) в растворах $HClO_4$. Определены основные параметры кинетики. Порядок процесса по амиде равен нулю, а по перхлорате церия непостаянный: ето подказывает протекание процесса по двум различным механизмам. На базе опытных данных вычислена энергия активации, которая в интервале 323-353 К равна 18,3 ккал/мол.

Представлен тоже простой аналитический метод количественного определения амида акриловой кислоты.