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OXIDATION REACTIONS OF NON-SATURATED DICARBOXYLIC ACIDS WITH CERIUM (IV) IN AQUEOUS SOLUTIONS OF PERCHLORIC ACID

Studies were carried out on reaction rates of citraconic, glutaconic and itaconic acids oxidation. An influence of concentration of particular reactans on these reaction rates has been determined by means of amperometric determination of cerium (IV) ions. Both, stoichiometry and the products of oxidation have been established. It was shown, that rate determining steps of the reactions mentioned above are determined by two stages with comparable rates. Activation energies of these steps have been determined in the case of all investigated acids. The most probable mechanism of oxidation of these acids has been proposed.

Oxidation reactions of dicarboxylic acids by means of strong oxidizers have been studied in numerous investigations [1-12].. It was pointed out, that ability for electrophilic atack of cerium (IV)ion is greater in the case, when the polarisation of bonds in acid molecule is increased. The presence of two methylenic groups in dicarboxylic acid molecule makes the polarisation such decreased that the oxidation by means of ceric perchlorate does not occur in practice [1] . An introduction of one or two hydroxyl groups in acid molecule provokes that the oxidation of derivatives of hydroxyacids runs much more easier [1,6-9]. The presence of double bond should increase the reducing properties, however this effect is less with regard to hydroxyl group.

Only a few investigations of oxidation of nonsaturated dicarboxylic acids with cerium perchlorate concern only the maleinic and fumaric acids [10-12]. In the light of the last sentence mentioned the investigation of both kinetics and mechanism of oxidation reactions of acids being upon our consideration citraconic, glutaconic and itaconic acids by means of cerium (IV) ions appears as a quite reasonable task. At last, it remains to be seen that the acids being considered by us differs to each other only in the placement of double bonds and carbonyl groups.

Experimental

Technique of measurements and reagents

The measurements of the rate of oxidation reaction of glutaconic, itaconic and citraconic acids by means of cerium (IV) were carried out at 333 K with the help of the method described earlier in preceding papers [13-14].

The current concentration of the oxidizing agent in the reaction has been determined amperometrically by indirect method with sodium oxalate and by the potentiometric method with iron (II)ammonium sulfate in the case, when a great excess of investigated acid was applied.

Cerium perchlorate solutions in perchloric acid were obtained according to the recipe by Smith and Getz [15].

Citraconic acid - pure of Fluka AG firm, was triply crystallized from the mixture of ether and ligroin, next dried at 333 K temperature.

Glutaconic acid - pure of Fluka AG firm, was triply crystallized from the mixture of ether and benzene and dried to constant mass at 333 K temperature.

Itaconic acid - pure of Loba-Chemie firm, was triply crystallized from water and dried to constant mass at 333 K temperature. Solutions of investigated compounds were prepared from weighed samples and their concentration was determined by alkacimetric titration.

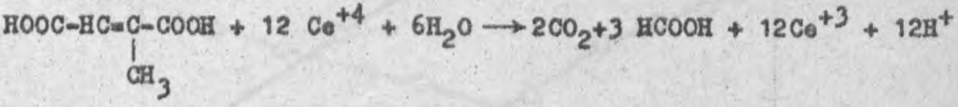
The chromatographic analysis of post - reaction mixtures was taken on GCMF 18.3 gas chromatograph on Porapack Q column at 323 K.

Results

The measurements enabling us to determine the stoichiometry of the reaction of oxidizing non-saturated dicarboxylic acids were carried out at 333 K temperature in 1.72 M solution of perchloric acid. The reaction products were identified chromatographicaly, it were carbon dioxide and formic acid in the case of each investigated acid. It has been established that the oxidation of citraconic acid is connected with 12-electron transformation while that of glutaconic one with 16-electron transformation. At last, the oxidation of itaconic acid is connected with 14-electron ore.

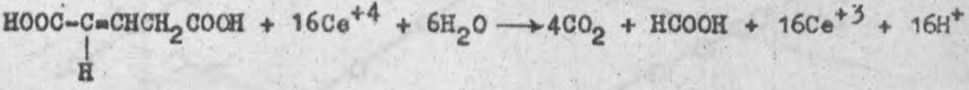
Thus, the oxidation reactions may be introduced in a following form:

citraconic acid:



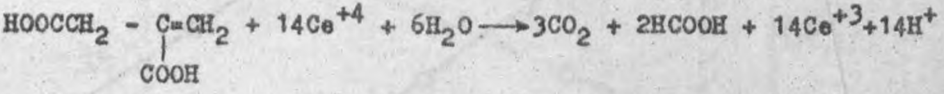
$$\mathrm{HOOC{-}HC{=}\underset{\underset{\displaystyle CH_3}{|}}{C}{-}COOH} + 12\ \mathrm{Ce^{+4}} + 6\mathrm{H_2O} \longrightarrow 2\mathrm{CO_2} + 3\ \mathrm{HCOOH} + 12\mathrm{Ce^{+3}} + 12\mathrm{H^+}$$

glutaconic acid:



$$\mathrm{HOOC{-}\underset{\underset{\displaystyle H}{|}}{C}{=}CHCH_2COOH} + 16\mathrm{Ce^{+4}} + 6\mathrm{H_2O} \longrightarrow 4\mathrm{CO_2} + \mathrm{HCOOH} + 16\mathrm{Ce^{+3}} + 16\mathrm{H^+}$$

itaconic acid:



$$\mathrm{HOOCCH_2} - \mathrm{\underset{\underset{\displaystyle COOH}{|}}{C}{=}CH_2} + 14\mathrm{Ce^{+4}} + 6\mathrm{H_2O} \longrightarrow 3\mathrm{CO_2} + 2\mathrm{HCOOH} + 14\mathrm{Ce^{+3}} + 14\mathrm{H^+}$$

The rate of reaction of oxidizing the acids was studied at various concentrations of reagents by the isolation method of Oswald in 1.72 M solution of $HClO_4$ at 333 K. The order of reaction in respect to a given acid was determined by the use of variable concentrations far from the stoichiometric ones and constant excess concentrations of cerium perchlorate. The order of reaction in respect to a cerium perchlorate was determined by the use of a great stoichiometric excess of investigated acids and variable, low concentrations of cerium perchlorate.

The results of measurements are presented on figs. 1-6 in the system of lg C_t as a function of time.

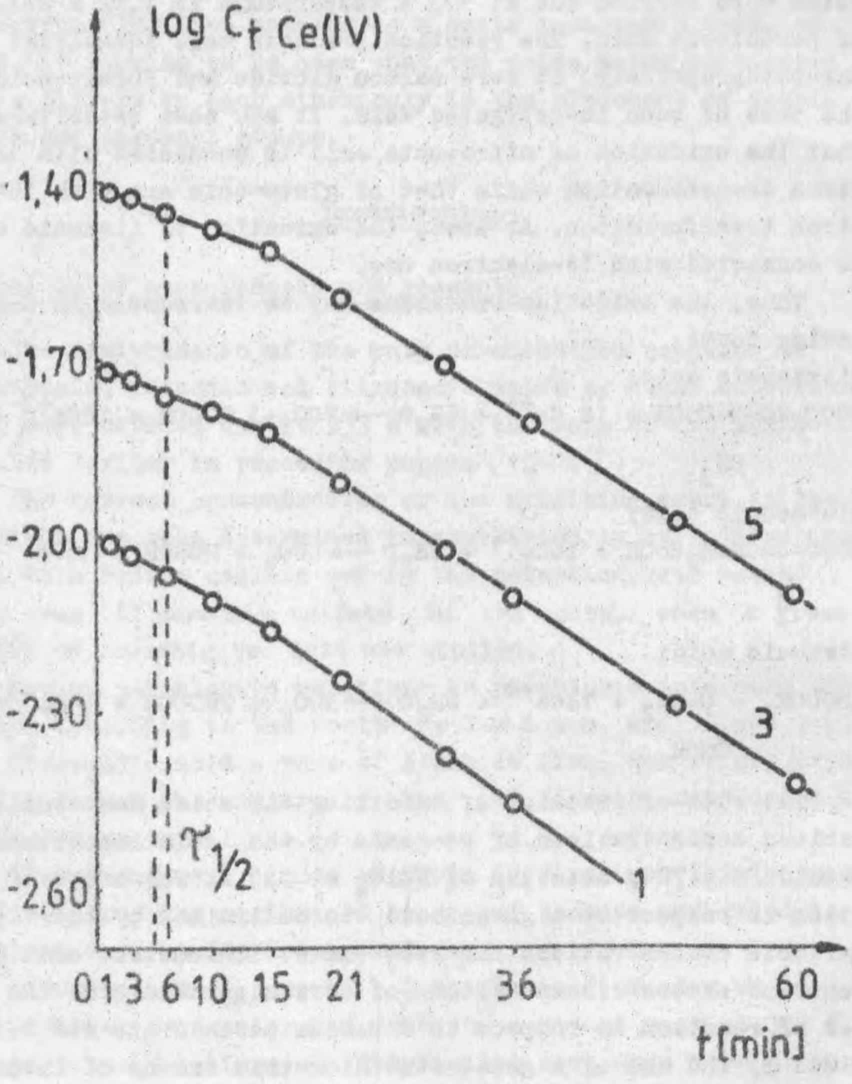


Fig. 1. Dependence lg $c_{Ce(IV)}$ = f(t) in oxidation reaction of citraconic acid (applied concentrations No. 1,3,5 - - table 1)

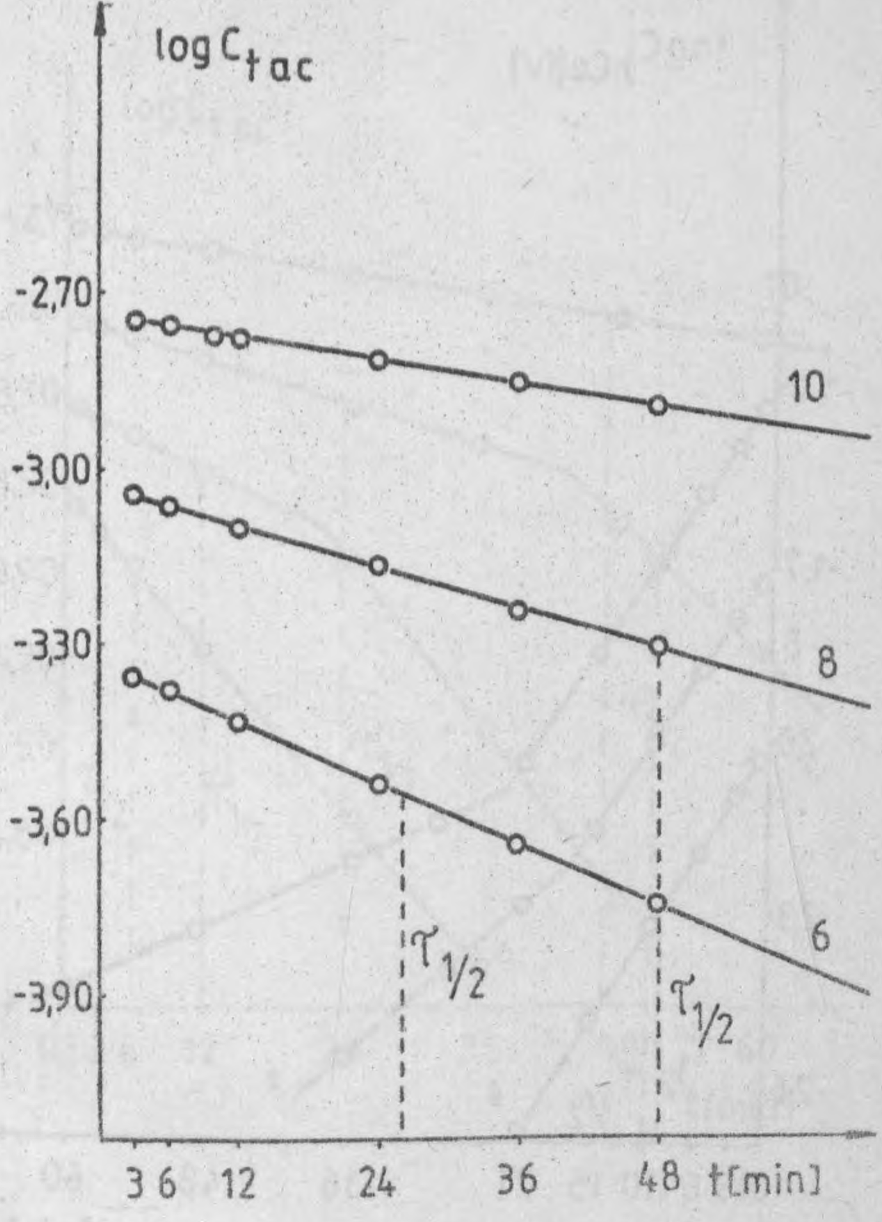


Fig. 2. Dependence $\lg c_{ac} = f(t)$ in oxidation reaction of citraconic acid (applied concentrations - No. 6,8,10 - table 1).

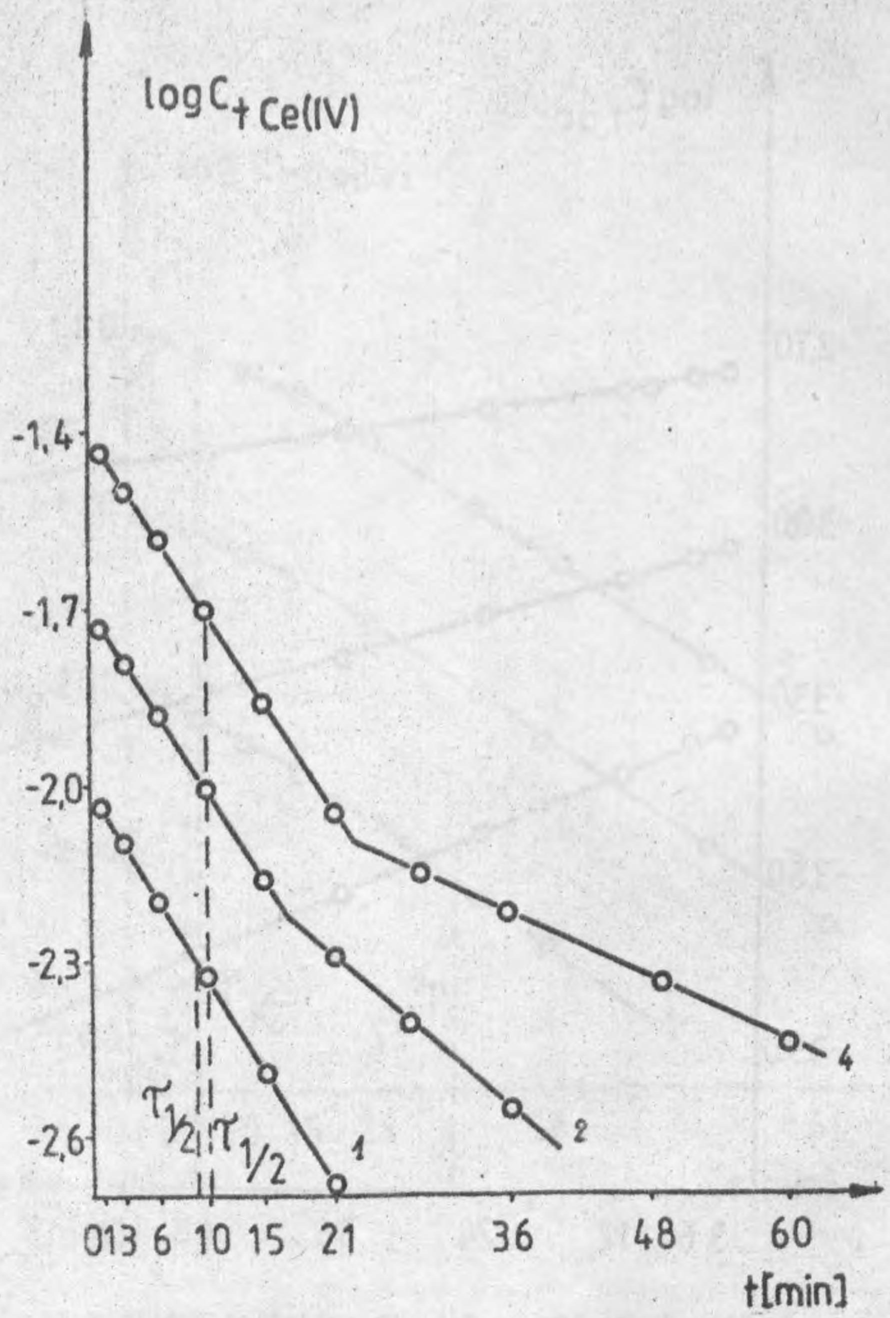


Fig. 3. Dependence lg $c_{Ce(IV)}$= f(t) in oxidation reaction of glutaconic acid (applied concentrations No. 1,2,4 - table 2).

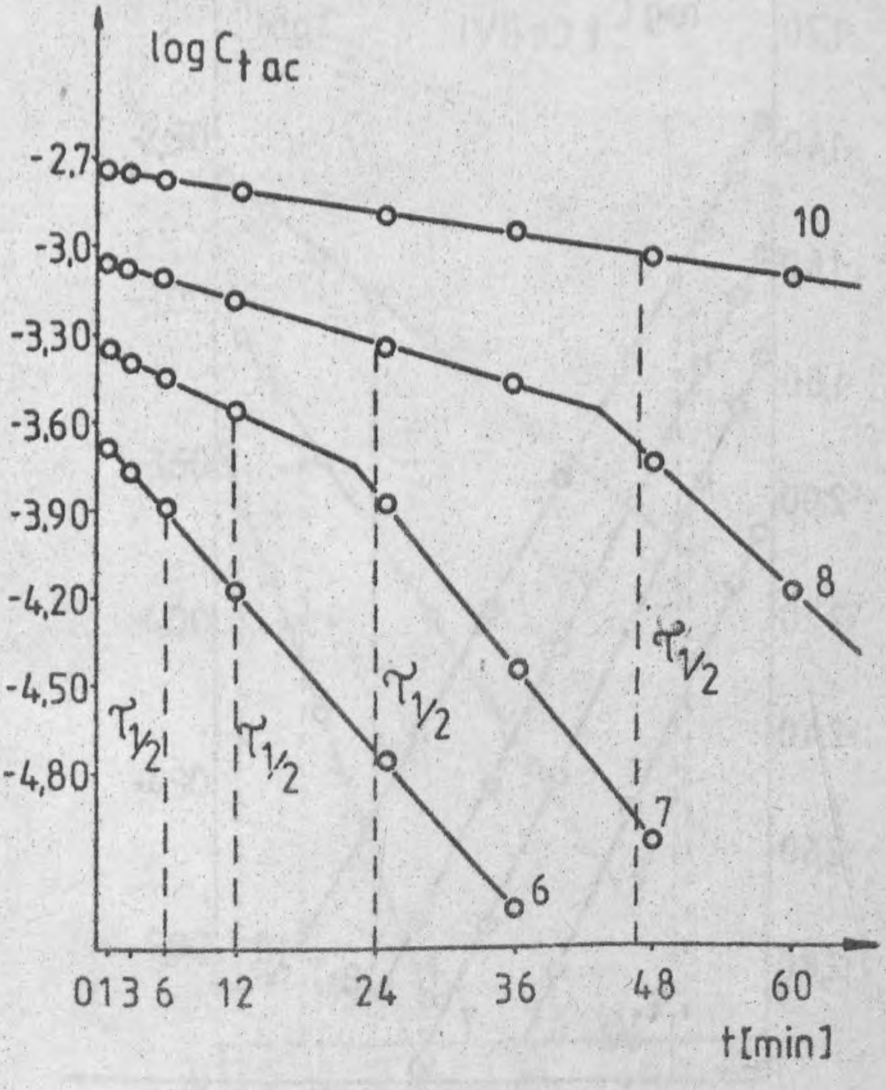


Fig. 4. Dependence $\lg_{ac} = f\ (t)$ in oxidation reaction of glutaconic acid (applied concentrations - No. 6,7,8,10 - table 2).

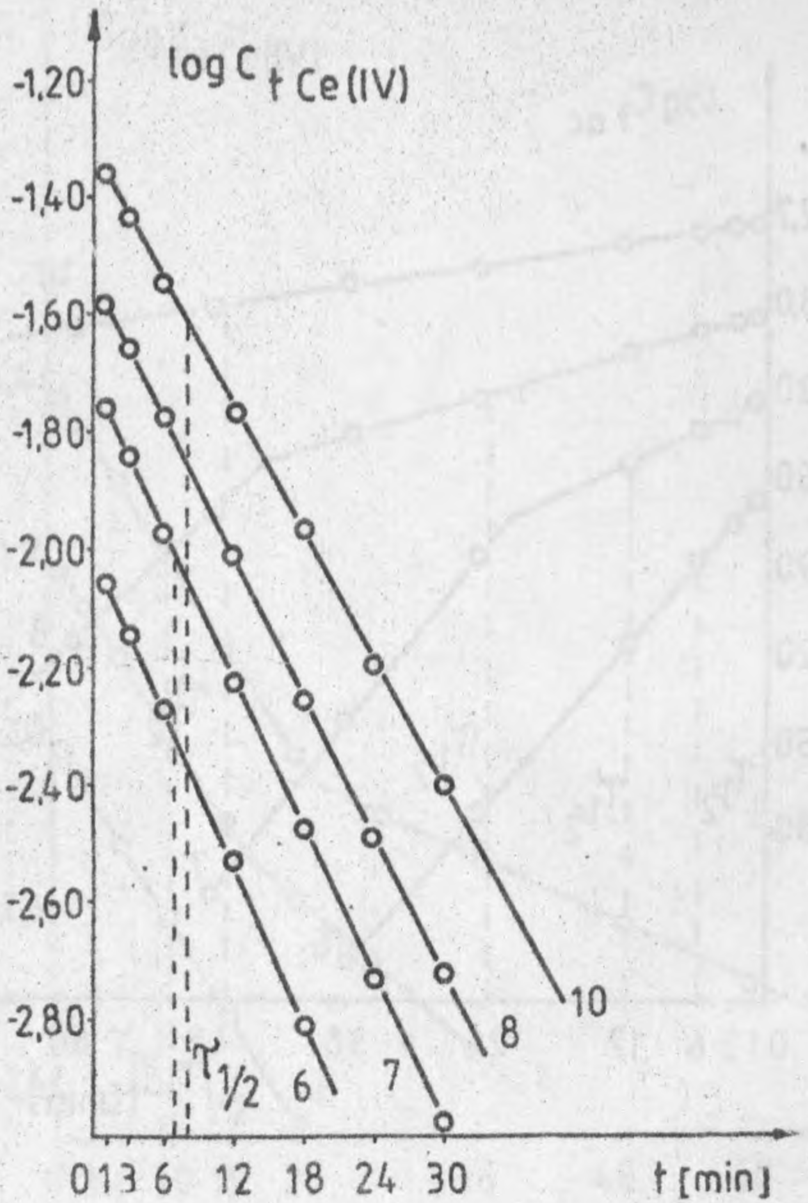


Fig. 5. Dependence lg $c_{Ce(IV)}$= f(t) in oxidation reaction of itaconic acid (applied concentrations No. 6,7,8,10 - table 3).

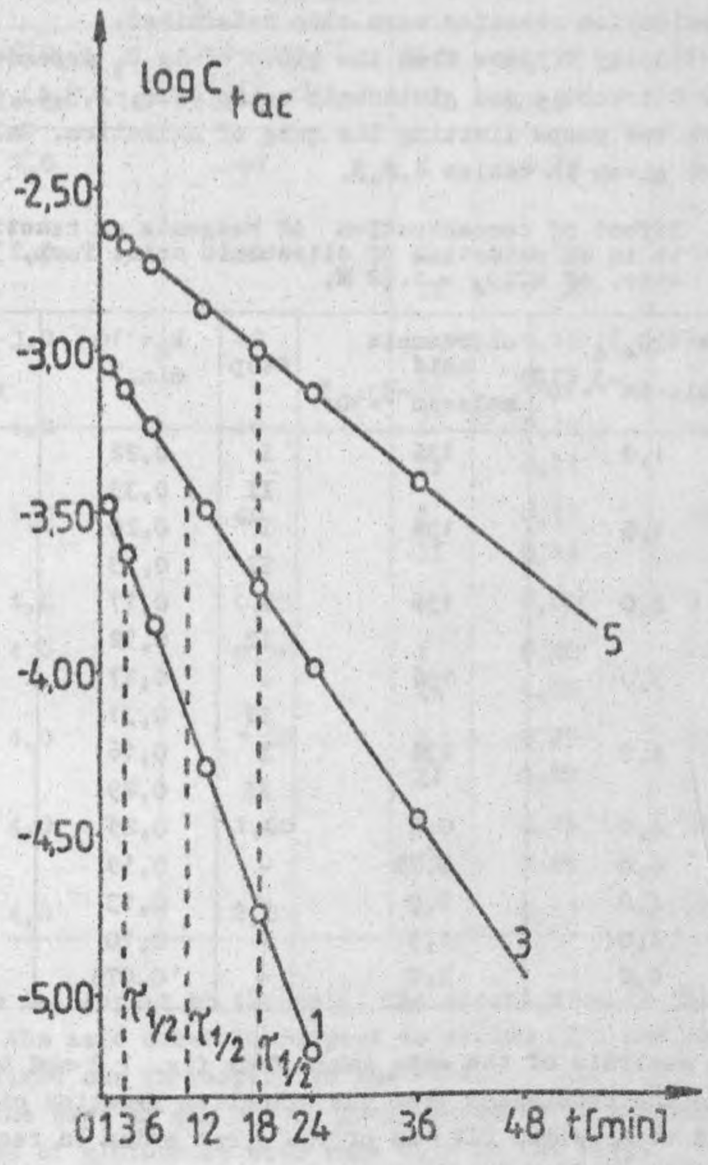


Fig. 6. Dependence $\lg c_{ac} = f(t)$ in oxidation reaction itaconic acid (applied concentrations - No. 1,3,5 - table 3).

The corresponding experimental rate constants and half-times of oxidation reaction were also determined.

It strictly follows from the plots of lg C_t dependence on time for citraconic and glutaconic acids (fig. 1,3,4) that there are two steps limiting the rate of oxidation. Calculations are given in tables 1,2,3.

Table 1. Effect of concentration of reagents on reaction rate in an oxidation of citraconic acid. Temp. 333 K, conc. of $HClO_4$ = 1.72 M.

No	$Ce(ClO_4)_4$ mole·dm^{-3}·10^2	citraconic acid mole·dm^{-3}·10^3	step	k_E· 10 min.$^{-1}$	$\tau_{1/2}$ min.
1	1,0	136	I	0,22	5
			II	0,33	
2	1,5	136	I	0,20	5
			II	0,33	
3	2,0	136	I	0,17	6
			II	0,32	
4	3,0	136	I	0,17	6
			II	0,31	6
5	4,0	136	I	0,16	6
			II	0,29	
6	4,0	0,5	-	0,25	26
7	4,0	0,75	-	0,19	37
8	4,0	1,0	-	0,13	48
9	4,0	1,5	-	0,10	70
10	4,0	2,0	-	0,075	92

The analysis of the data taken from fig. 1,2 and table 1 leads to the conclusion that the oxidation reaction of citraconic acid with cerium (IV) is of the first order in respect to the oxidizer and of the zero one in respect to the reductor. The oxidation runs in two steps, the first step is slower than the second one. The results of the kinetic investigations for glutaconic acid (fig. 3,4, tabl. 2) indicate also two steps in the runing of the oxidation. The first step is the reaction of the first order in respect to cerium (IV) and that is of the

Table 2. Effect of concentration of reagents on reaction rate in an oxidation of glutaconic acid. Temp. 333 K, conc. of $HClO_4$ = 1,72 M.

No	$Ce(ClO_4)_4$ mole·dm^{-3}·10^2	glutaconic acid mole·dm^{-3}·10^3	step	k_E·10 min.$^{-1}$	$\tau_{1/2}$ min.
1	1,0	40	I	0,79	9
			II	-	-
2	2,0	40	I	0,79	10
			II	0,38	
3	3,0	40	I	0,78	10
			II	0,27	
4	4,0	40	I	0,78	10
			II	0,21	
5	5,0	40	I	0,78	10
			II	0,16	
6	4,0	0,25	-	0,89	6
7	4,0	0,50	I	0,48	12
			II	0,89	
8	4,0	1,00	I	0,25	24
			II	0,87	
9	4,0	1,50	I	0,19	35
			II	0,86	
10	4,0	2,0	-	0,13	46

zero one in respect to the acid. The second step is the reaction of the zero order in respect to cerium (IV) and that is of the first one in respect to the acid.

In the case of the use of great excesses of reagents the oxidation of glutaconic acid runs only in one step.

The oxidation reaction of itaconic acid is of the first order in respect to the oxidizer and of the zero one in respect to the reductor and in the range of possible for obtaining concentrations no steps took place.

The influence of the temperature on the rate of oxidation

Table 3. Effect of concentration of reagents on reaction rate in an oxidation of itaconic acid. Temp. 333 K, conc. of $HClO_4$ = 1,72 M.

No	$Ce(ClO_4)_4$ mole·dm^{-3}·10^2	itaconic acid mole·dm^{-3}·10^3	k_E min.$^{-1}$	$\tau_{1/2}$ min.
1	4,0	0,25	0,263	3
2	4,0	0,50	0,147	5
3	4,0	1,00	0,074	10
4	4,0	1,50	0,058	14
5	4,0	2,00	0,040	18
6	1,0	25,0	0,93	7
7	2,0	25,0	0,92	7
8	3,0	25,0	0,92	7
9	4,0	25,0	0,91	8
10	5,0	25,0	0,91	8

reaction of non-saturated dicarboxylic acids has been studied for reaction mixtures of the following composition: $4,0\cdot10^{-2}$M of $Ce(ClO_4)_4$, 1,72 M of $HClO_4$ and $1\cdot10^{-3}$M of investigated acid at 318 K, 333 K and 348 K temperatures. These measurements has allowed to determine the activation energies of the stages limiting the rate of oxidation.

The energies are:

For citraconic acid:

I step E_A = 57,2 ±1 kJ/mole

II step E_A = 43,1 ±0,4 kJ/mole

For glutaconic acid:

I step E_A = 47,6 ±0,6 kJ/mole

II step E_A = 38,7 ±0,4 kJ/mole

For itaconic acid:

E_A = 34,7 ±0,2 kJ/mole

Discussion of results

The kinetic data for citraconic, glutaconic and itaconic acids show the mechanism of these reaction enough complicated. We may distinguish two rate determining steps the course of oxidation reaction of comparable rates.

Assuming, that one step is an oxidation of initial acid and the second one is an oxidation of the intermediate product being obtained from the substrate in a n-electron transformation we obtain the following kinetic equation describing the course of the reaction:

$$\frac{-d}{dt}\ C_{Ce(IV)} = k_1 C_{Ce(IV)} \cdot C_{ac} + k_2 C_{Ce(IV)} \cdot C_{ip} \qquad (1)$$

where:

$C_{Ce(IV)}$ - concentration of Ce(IV) in a given moment t

C_{ac} - concentration of the acid a given moment t

C_{ip} - concentration of the intermediate product a given moment t

Puting in (1)

$$C_{ac} = C^o_{ac} - \frac{1}{n}\left(C^o_{Ce(IV)} - C_{Ce(IV)}\right)$$

$$C_{ip} = \frac{1}{n}\left(C^o_{Ce(IV)} - C_{Ce(IV)}\right)$$

where $C^o_{Ce(IV)}$ and C^o_{ac} stand for initial concentrations of cerium(IV)ions and the acid, respectively.

We obtain:

$$\frac{-d\ C_{Ce(IV)}}{dt} = C_{Ce(IV)}\left(k_1 C^o_{ac} - k_1 \frac{1}{n} C^o_{Ce(IV)} + k_2 \frac{1}{n} C^o_{Ce(IV)}\right) + C_{Ce(IV)}\frac{1}{n}\left(k_1 - k_2\right) \qquad (2)$$

Integrating eq (2) with regard to boundary conditions we get:

$$\ln C_{Ce(IV)} = \ln\left\{\frac{C^{o}_{Ce(IV)}}{k_1 C^{o}_{ac}}\left[k_1\left(C^{o}_{ac} - \frac{C^{o}_{Ce(IV)}}{n}\right) + \left(\frac{k_1 - k_2}{n}\right) C_{Ce(IV)} + \frac{k_2 C^{o}_{Ce(IV)}}{n}\right]\right\} - t\left[k_1\left(C^{o}_{ac} - \frac{C^{o}_{Ce(IV)}}{n}\right) + \frac{k_2\, C^{o}_{Ce(IV)}}{n}\right] \qquad (3)$$

Because the isolation method of Ostwald was used for obtaining the kinetic data we may discuss only the limiting cases of the equation (3).

I case: $C^{o}_{ac} \gg \frac{C^{o}_{Ce(IV)}}{n}$ – equation (3) may be simplified to a form:

$$\ln C_{Ce(IV)} = \ln\left\{\frac{C^{o}_{Ce(IV)}}{k_1 C^{o}_{ac}}\left[k_1 C^{o}_{ac} + \left(\frac{k_1 - k_2}{n}\right) C_{Ce(IV)}\right]\right\} - \left(k_1 C^{o}_{ac} + \frac{k_2\, C^{o}_{Ce(IV)}}{n}\right) t \qquad (3a)$$

II case: $C^{o}_{ac} \ll \frac{C^{o}_{Ce(IV)}}{n}$ instead of eq (3) we may write a following expression:

$$\ln C_{Ce(IV)} = \ln \frac{C^{o}_{Ce(IV)}}{n k_1\, C^{o}_{ac}}\left[(k_2 - k_1) + \left(C^{o}_{Ce(IV)} - C_{Ce(IV)}\right)\right] - \frac{C^{o}_{Ce(IV)}}{n}(k_2 - k_1)\; t \qquad (3b)$$

The above equations are explaining the obtained kinetic data and also the plots of lg C_t dependence on time.

Citraconic acid

The plot of lg $C_{Ce(IV)}$ as a function of time (fig.1) in the case of $C^{o}_{ac} \gg \frac{1}{n} C^{o}_{Ce(IV)}$ one can explain analysing the equation (3a). In a initial course of the reaction, for a small values of t both logarithmic terms of that equation make considerable changes of lg C_t values. Becouse k_2 is greater than k_1, the logarithmic term rises, while the concentration of cerium(IV) decreases, at the same time, the second term of the equation diminishes. This case corresponds to the first sector with a smaller inclination. Along with the lapse of time of the reaction the second term of the equation becomes prevailing, in general.

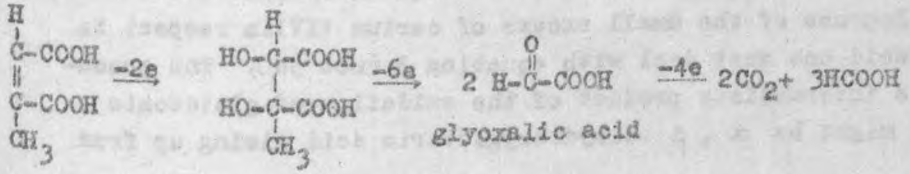
One may observe on the graph a sector with a greater inclination which corresponds to the equation:

$$\ln c_{Ce(IV)} = \mathrm{const} - \left(k_1 c^{o}_{ac} + \frac{1}{n} k_2 c^{o}_{Ce(IV)}\right) t$$

In the case of the excess of Ce(IV)with regard to the acid the zero order of the reaction in respect to the reductor may be observed. It is in agreement with equation (3b). The logarithmic term depends upon the acid concentration only in the initial corse of the reaction and the expression $(c^{o}_{Ce(IV)} - c_{Ce(IV)})$ goes swiftly to c^{o}_{ac} value. The second term of that equation is independent on acid concentration, so it means, that beyond the initial course of reaction the rate of oxidation is the zero order in respect to the reductor.

The analysis of (3a) equation in the imit of great concentrations of c^{o}_{ac} leads to an unexpected conclusion, that, in this case the rate of the reaction should be proportional to the initial concentration of citraconic acid. In order to check this supposition the additional series of measurements was done. The constant concentrations of ceric perchlorate and also variable ones being in a great excess in respect to stoichiometric concentrations of the acid have been taken into account. The results, shown in table 4, confirm the equity of the adopted assumptions concerning the mechanism of the process.

Therefore, mentioning the above results and discussion one can accept the probable mechanism of the oxidation of citraconic acid:



$$\begin{matrix}\mathrm{H}\\ |\\ \mathrm{C\text{-}COOH}\\ \|\\ \mathrm{C\text{-}COOH}\\ |\\ \mathrm{CH_3}\end{matrix} \xrightarrow{-2e} \begin{matrix}\mathrm{H}\\ |\\ \mathrm{HO\text{-}C\text{-}COOH}\\ |\\ \mathrm{HO\text{-}C\text{-}COOH}\\ |\\ \mathrm{CH_3}\end{matrix} \xrightarrow{-6e} 2\ \mathrm{H\text{-}\overset{\overset{O}{\|}}{C}\text{-}COOH} \xrightarrow{-4e} 2CO_2 + 3HCOOH$$

methyltartaric acid

Table 4. Effect of initial concentration of citraconic acid on reaction rate in an oxidation by cerium (IV). Temp. 333 K, $Ce(ClO_4)_4 = 4,0 \cdot 10^{-2}$ M, $HClO_4 = 1,72$ M.

No	citraconic acid mole $\cdot dm^{-3} \cdot 10^2$	$k_E \cdot 10$ $min.^{-1}$
1	6,4	0,07
2	12,8	0,14
3	25,6	0,29
4	38,4	0,43
5	51,2	0,52

The atack of Ce(IV) ion on citraconic acid molecule and the first stage of the oxidation of methyltartaric acid should be regarded as the two rate determining steps of oxidation.

Glutaconic acid

The obtained kinetic relationships one can explain in a similar way as it was done in the case of citraconic acid assuming that two limiting steps with comparable rates are present, where $k_1 > k_2$.

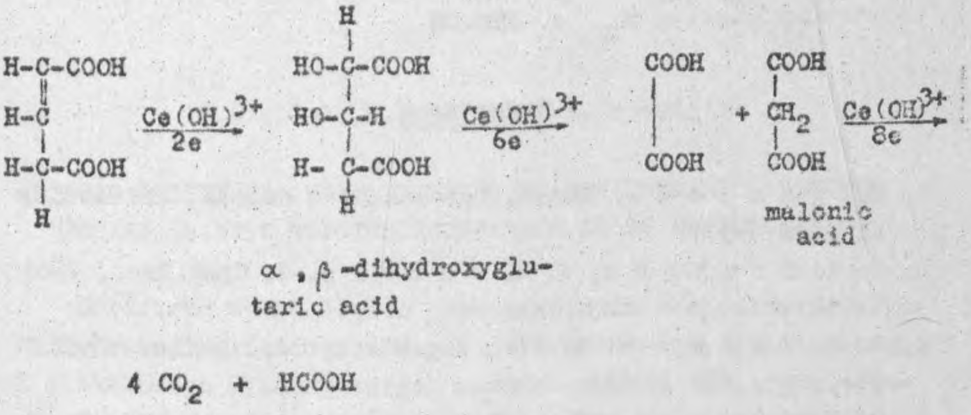
The analysis of equation (3a) shows, that for $k_1 > k_2$ both logarithmic terms of the equation decrease in time, provoking that in the initial course of the reaction, the sector with a smaller inclination corresponding to the reaction of the first order in respect to cerium (IV) is being observed (fig. 3).

When the logarithmic term stops to vary in practice, the sector with a greater inclination corresponding to the reaction of the zero order in respect to cerium (IV) may be observed on the graph. The zero order of reaction in respect to glutaconic acid being observed on fig. 4 can be substantiated such as it was done in the case of citraconic acid.

Becouse of the small excess of cerium (IV) in respect to the acid one must deal with equation 3 (not 3b). The presumable intermediate product of the oxidation of glutaconic acid might be α, β -dihydroxyglutaric acid rising up from the addition of two hydroxyl groups to double bond carbon-carbon. The additional investigations have showed, that α , β -dihydroxyglutaric acid is oxidized by Ce(IV)ions in a 14-electron transformation forming 4 molecules of formic acid. The partial order of the reaction in respect to that acid is equal to one and activation energy of the value 40 ±0,7 kJ/mol is smaller then E_A of the glutaconic acid. Thus, the α , β -dihydroxyglutaric acid may stand for the intermediate product. The next of the intermediate products can be the malonic acid being oxidized by Ce(IV) in a 6-electron transformation forming 2 molecules of CO_2 and 1 molecule of HCOOH.

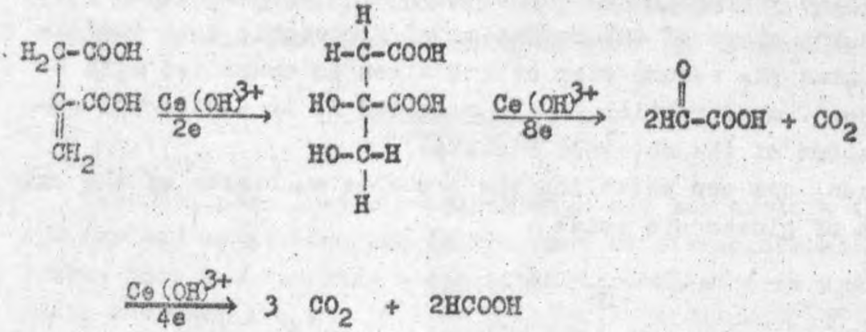
The partial order of the oxidation reaction by means of Ce(IV) ions in respect to malonic acid is equal to one and activation energy is 36 kJ/mol [1]. The electronicity of particular steps of the oxidation of glutaconic acid indicating, that the second step of oxidation is connected with 8-electron transformation may be regarded as an additional confirmation of the obtained results.

Thus, one can establish the probable mechanism of the oxidation of glutaconic acid:



Itaconic acid

The kinetic relationship obtained for itaconic acid are similar to ones obtained for the acids previously considered. One can not observe the characteristic collapses on the graphs (fig. 5,6). It is caused by considerably greater rate of the oxidation of itaconic acid. In this case, the logarythmic term of equation (3a) goes to zero faster and it is not possible to observe experimentally the initial sector with a smaller inclination. The probable mechanism of the oxidation reaction of itaconic acid by means of Ce(IV) ions involving the rising of the derivative of dihydroxyacid in the first stage and also the results of preceding investigations of Ignaczak [1] may be introduced in a following way:



$$H_2C(COOH)-C(COOH)=CH_2 \xrightarrow[2e]{Ce(OH)^{3+}} H-\overset{H}{C}(COOH)-C(OH)(COOH)-\underset{H}{C}(OH)-H \xrightarrow[8e]{Ce(OH)^{3+}} 2H\overset{O}{\overset{\|}{C}}-COOH + CO_2$$

$$\xrightarrow[4e]{Ce(OH)^{3+}} 3\ CO_2 + 2HCOOH$$

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REAKCJE UTLENIANIA NIENASYCONYCH KWASÓW DWUKARBOKSYLOWYCH JONAMI Ce(IV)W WODNYCH ROZTWORACH KWASU NADCHLOROWEGO

Określono wpływ stężeń poszczególnych reagentów na szybkość reakcji utleniania kwasów: cytrakonowego, glutakonowego i itakonowego wykorzystując amperometryczne oznaczanie jonów Ce(IV). Wyznaczono stechiometrię oraz ustalono produkty utleniania. Wykazano, iż reakcje te są procesami, w których stadia limitujące określone są przez dwa etapy o porównywalnej szybkości. Wyznaczone zostały energie aktywacji tych etapów w przypadku badanych obiektów oraz zaproponowano prawdopodobny mechanizm reakcji utleniania kwasów.