

Sabina Cieplak, Maksymilian Ignaczak and Andrzej Grzejdzia

OXIDATION REACTIONS OF CIS- AND TRANS-ACONITIC ACIDS WITH
CERIUM (IV) IONS IN AQUEOUS SOLUTIONS OF PERCHLORIC ACID

The stoichiometry and products of oxidation have been determined. Kinetics of oxidation reactions of cis- and trans-aconic acid was investigated. By means of Ostwald's method the partial orders of the reaction were determined. It was shown, that the oxidation runs in two rate determining steps where the one of these steps may be regarded as a transformation occurring without participation cerium (IV) ions. Also activation energies of these steps have been determined. The most probable mechanism of oxidation of these compounds was proposed.

Investigations of an oxidations of carboxylic acids by means of cerium (IV) perchlorate [1-6] prove, that these processes proceed easier in the presence of hydroxylic and carboxylic groups or a double bond in acid molecule.

For example, oxalic acid reacts with cerium (IV) perchlorate immediately at room temperature, while the glycolic one in the same conditions reacts slower and the oxidation of acetic acid does not proceed in practice [1,7].

Likewise, glutaconic acid is oxidized with cerium (IV) ions relatively easily, while the glutaconic one does not undergo any transformation [1,8].

The investigations of non-saturated dicarboxylic acids prove, that their oxidations runs through two rate determining steps, during the addition of two hydroxyl groups to a double bond at the initial stage [8].

Only one tricarboxylic acid which has been investigated in the course of an oxidation reaction with cerium (IV) sulphate was the citric one. That process runs with the formation of both unstable intermediate complex and free radicals [2,3,9].

We took upon our investigations isomers of cis- and trans-acconitic acid which differ from the citric acid by the presence of a double bond and the absence of one hydroxyl group.

Experimental

Reagents and the measurements technique

Cerium (IV) perchlorate solution in perchloric acid was obtained from cerium (IV)-ammonium nitrate according to the recipe of Smith and Getz [10].

Cis-acconitic acid - pure - of British Houses Ltd., BDH Laboratory Chemical Division was triply crystallized from hot, triply distilled water with an active carbon and then dried to a constant mass at 333 K. Melting point of the final product was 398 K.

Trans-acconitic acid - pure - of Koch-Light Laboratories Ltd., Colnbrook - Bucks, England production was purified by triple crystallization from hot, triply distilled water with an active carbon, then dried to a constant mass at 333 K. Melting point of the final product was 467 K.

The solutions of acids in question were prepared from weighed samples, their concentrations were determined alkalimetrically.

The measurements of the rate of cerium (IV) ions reactions with acconitic acids were carried out at 333 K temperature by the method described in previous papers [11-12].

The concentration of cerium (IV) ions in the course of reaction has been determined amperometrically or by potentiometric method described earlier in paper [8].

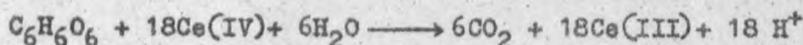
The chromatographic investigations of post-reaction mixtures were made on GCFH 183 gas chromatograph with the Parapack Q column at 323 K temperature.

Results

The stoichiometry of oxidation reaction of cis- and trans-acconitic acids with cerium (IV) ions was determined at 333 K

in 1,72 M solution of perchloric acid in the presence of sixty-fold molar excess of the oxidizer. Using the chromatography as an identification method it was pointed out that the carbon dioxide was the only one product of the reaction.

It has been established that the oxidation of these two acids is connected with 18-electron transformation, so one can introduce the following scheme for that oxidation process:



Some attempts were made in order to determine the general order of the reaction (stoichiometric quantities of both oxidizer and reductor according to their equivalent concentrations have been applied in 3M solution of $HClO_4$ at 333 K). In the case of cis-aconitic acid, these attempts have shown that the rate of oxidation of this compound at the above ratio of concentrations is transient.

Because of the above fact it was impossible to make investigations with a satisfactory accuracy; Hence, only the general order of the oxidation of trans-aconitic acid with cerium (IV) ions has been determined.

The results of the measurements leading to the determination of the general order of trans-aconitic acid oxidation are plotted on Fig. 1 in a system: $lg c_t Ce(IV)$ as a function of time.

The partial orders of reaction in respect to acid upon investigation and also in respect to cerium (IV) ions for cis- and trans-aconitic acids have been determined by means of an isolation method of Ostwald in 1,72 M solution of $HClO_4$ at 333 K temperature. The results of measurements are presented of fig. 2-5 in a system: $lg c_t = f(t)$.

The corresponding rate constants and half times of the reactions have been also calculated. In some measurements seria the plots of $lg c_t$ dependence on time show in a distinct way, that there are two rate determining steps of oxidation. The results of calculations are presented in tables 1 and 2.

The run of parallel lines and also the values of rate constants and half-times prove, that the general order of oxidation reaction of trans-aconitic acid with cerium(IV) ions is

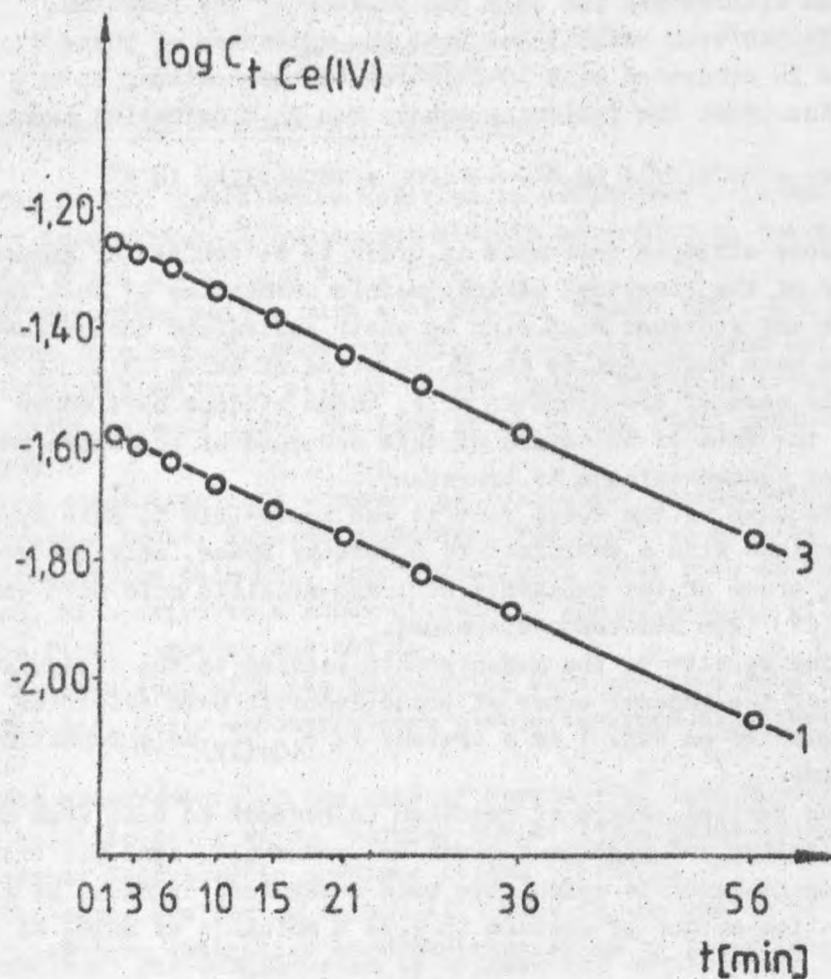


Fig. 1. The dependence of $\lg C_{\text{Ce(IV)}} = f(t)$ in the oxidation reaction of trans-aconitic acid for a stoichiometric ratio of cerium (IV) ions and acid concentrations (applied concentrations - No. 1,3 - table 1).

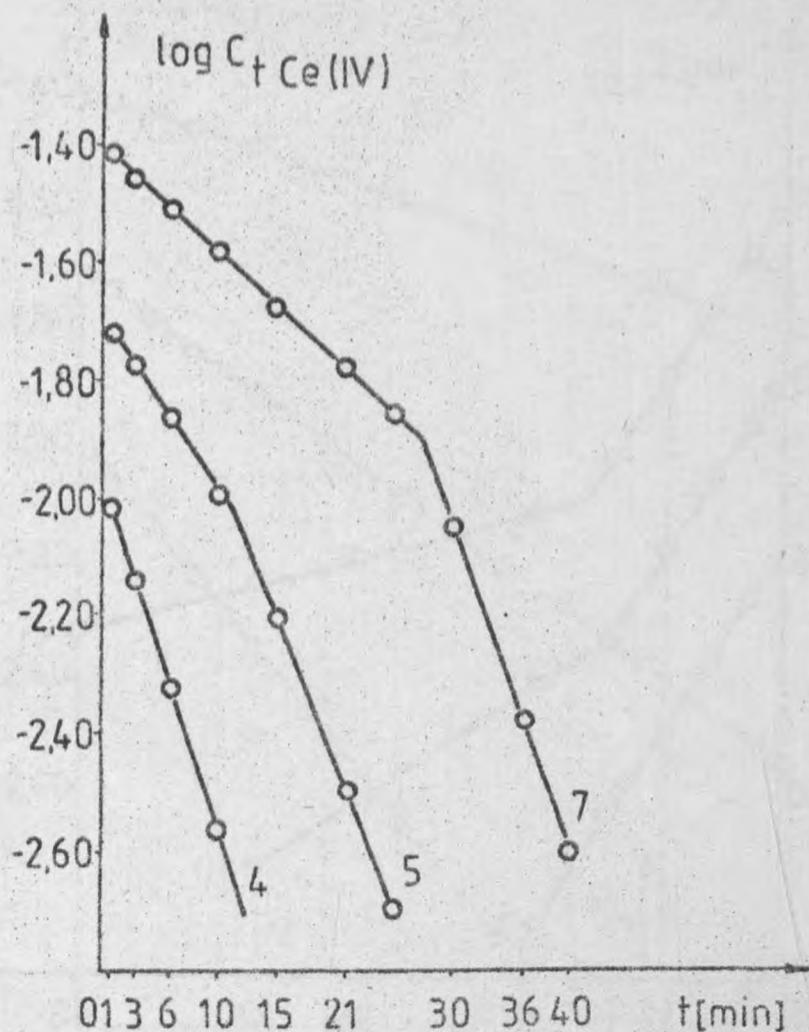


Fig. 2. The dependence of $\lg C_{\text{Ce(IV)}} = f(t)$ in the oxidation reaction of trans-aconitic acid (applied concentrations - No. - 4, 5, 7 - table 1).

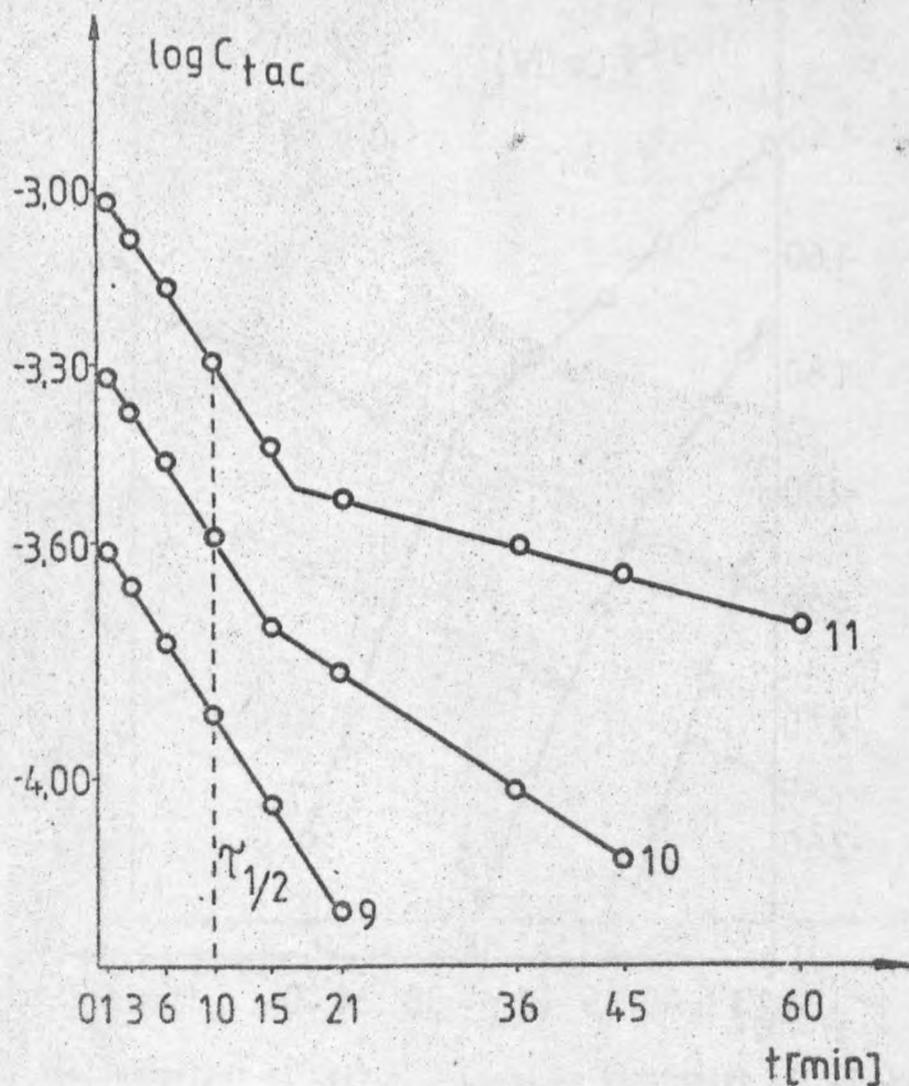


Fig. 3. The dependence of $\lg c_{ac} = f(t)$ in the oxidation reaction of trans-aconitic acid (applied concentrations - No. 9, 10, 11 - table 1).

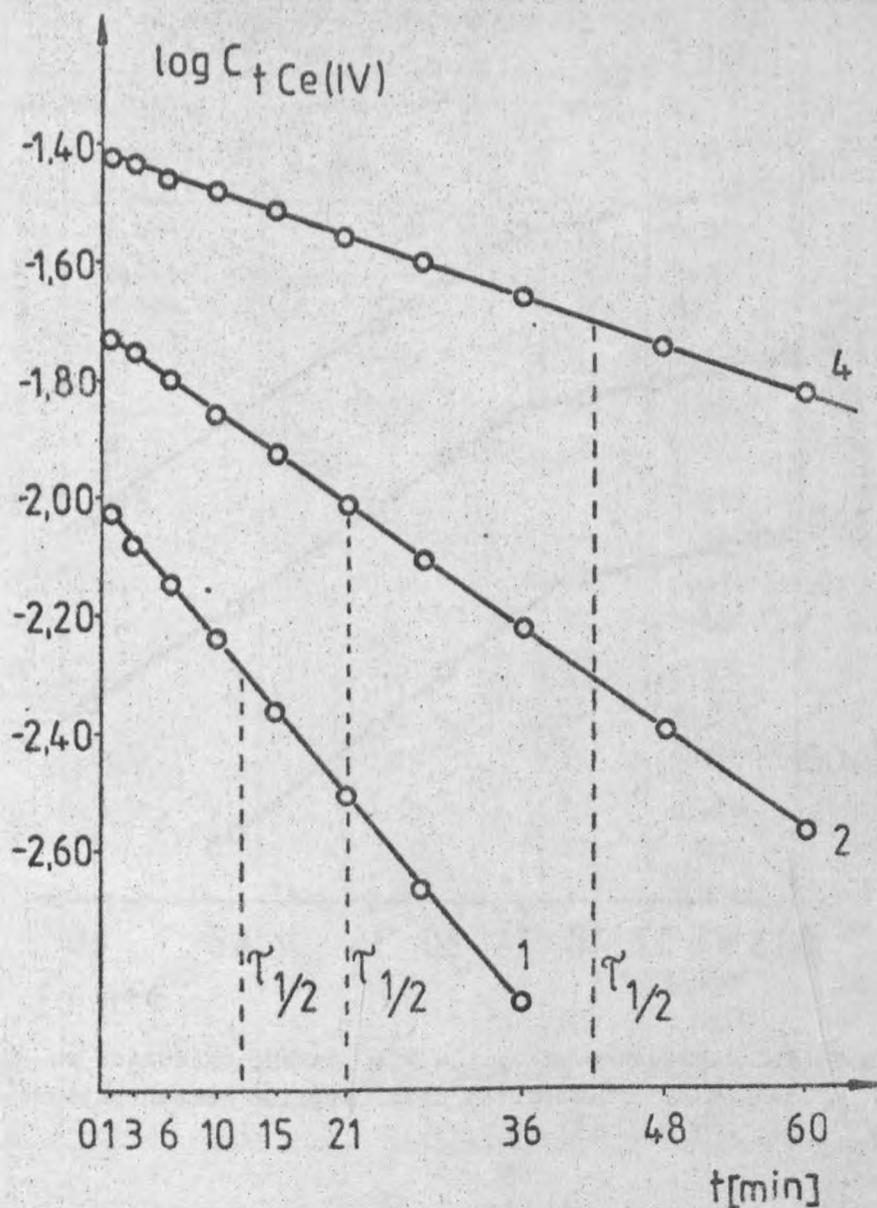


Fig. 4. The dependence of $\lg C_{\text{Ce(IV)}} = f(t)$ in the oxidation reaction of cis-aconitic acid (applied concentrations - No. 1, 2, 4 - table 2).

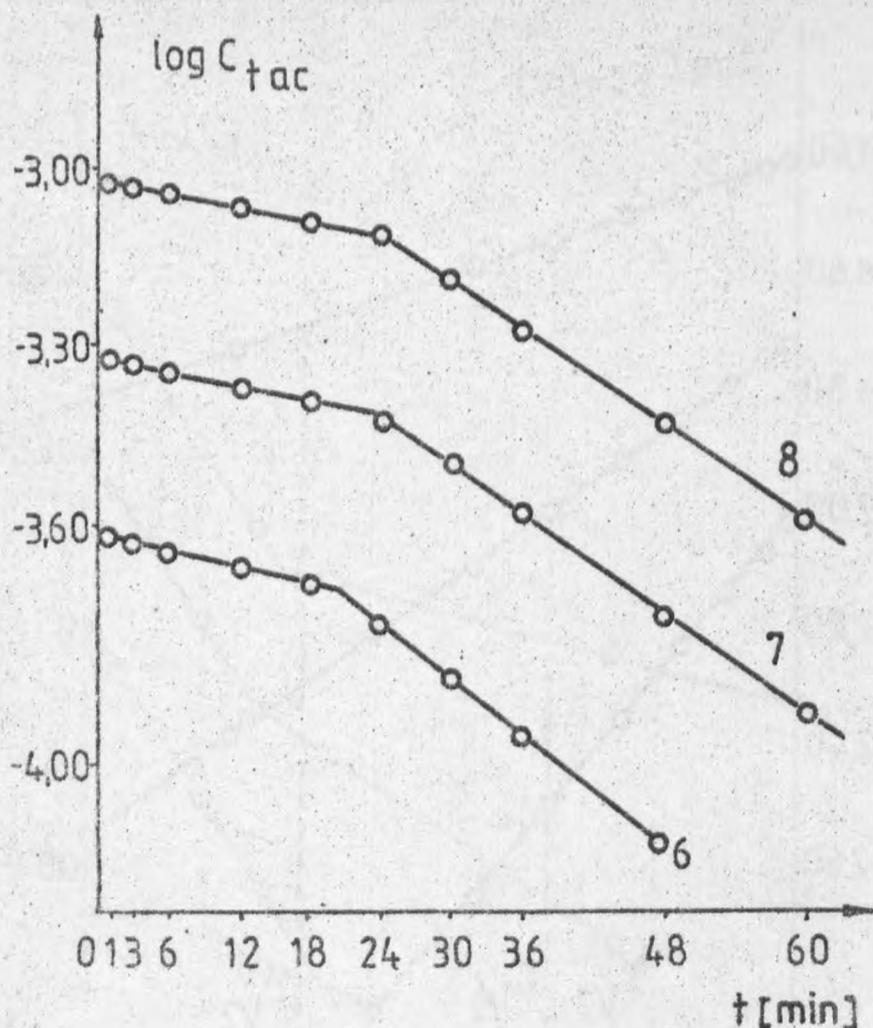


Fig. 5. The dependence of $\lg c_{ac} = f(t)$ in the oxidation reaction of cis-aconitic acid (applied concentrations - No. 6, 7, 8 - table 2).

equal to 1. At the excess concentration of any reagent, one can see on the plots $\lg c_t = f(t)$ the characteristic collapses confirming two step reaction. Basing on data in table 1 one may come to conclusion that in the step the order of reaction in respect to cerium (IV) ions is equal 1 when, in respect to

Table 1. An influence of reagent concentrations on the rate of oxidation of trans-aconitic acid. Temp. 333 K, 1,72 M HClO₄.

No	Ce ClO ₄ 4 mol·dm ⁻³ ·10 ²	trans-aconitic acid mol·dm ⁻³ ·10 ³	step	k _F min. ⁻¹	τ _{1/2} min.
1	2,696	1,50	-	0,020	37
2	4,044	2,25	-	0,021	36
3	5,402	3,00	-	0,021	36
4	1,0	30,0	I	0,122	6
5	2,0	30,0	I	0,066	10
			II	0,121	6
6	3,0	30,0	I	0,049	14
			II	0,121	6
7	4,0	30,0	I	0,034	20
			II	0,120	6
8	5,0	30,0	I	0,026	27
			II	0,120	6
9	4,0	0,25	I	0,070	10
10	4,0	0,50	I	0,070	10
			II	0,031	22
11	4,0	1,00	I	0,069	10
			II	0,014	49
12	4,0	1,50	I	0,069	10
			II	0,008	87
13	4,0	2,00	I	0,068	10
			II	0,004	173

acid is equal 0. In the case of cis-aconitic acid the measurements show, that the partial order of reaction in respect to cerium (IV) ions is equal 0 (fig. 1, No. 1-5 - table 2). However, when there is an excess of oxidizer, the run of curves $\lg c_t = f(t)$ (fig. 5) and also values of k_F and $\tau_{1/2}$

Table 2. An influence of reagent concentrations on the rate of oxidation of cis-aconitic acid. Temp. 333 K, 1,72 M HClO₄

No	Ce(ClO ₄) ₄ mol·dm ⁻³ ·10 ²	cis-aconitic acid mol·dm ⁻³ ·10 ³	step	k _E ·10 ⁻¹ min. ⁻¹	1/2 min.
1	1,0	30,0	-	0,57	12
2	2,0	30,0	-	0,32	21
3	3,0	30,0	-	0,23	32
4	4,0	30,0	-	0,16	42
5	5,0	30,0	-	0,13	52
6	4,0	0,25	I	0,088	79
			II	0,31	22
7	4,0	0,50	I	0,087	80
			II	0,30	23
8	4,0	1,00	I	0,087	80
			II	0,29	24
9	4,0	1,50	I	0,086	81
			II	0,29	24
10	4,0	2,00	I	0,085	81
			II	0,30	23

(No. 6-10, table 2) show, that the oxidation of cis-aconitic acid with cerium (IV) ions proceeds in a two steps with different rates and it is the first order reaction in respect to acid.

An influence of the temperature on rate of reactions in question has been determined with the help of solutions of the content: 4,0·10⁻² M Ce(ClO₄)₄, 1,0·10⁻³ M acid, 1,72 M HClO₄ at temperatures 318, 333 and 348 K.

These measurements allowed to determine activation energies of stages limiting the rate of oxidation. They are:

for cis-aconitic acid I step E_A = 52,7 ± 0,5 kJ/mole

II step E_A = 44,9 ± 0,8 kJ/mole

for trans-aconitic acid I step $E_A = 44,3 \pm 0,8$ kJ/mole
 II step $E_A = 33,8 \pm 1,0$ kJ/mole

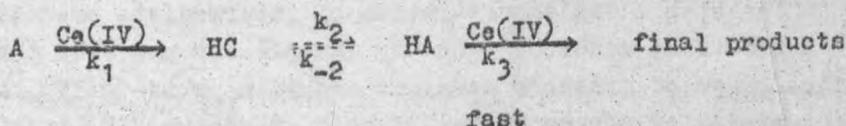
Discussion of results

The kinetics parameters of oxidation process of cis- and trans-aconitic acids (zeroth order of reaction in respect to cerium ions and the first one in respect to reductor) show, that one of the steps limited the rate of reaction is a transformation of intermediate product occurring without participation of cerium ions.

Because the transformation of the initial aconitic acids in a solution, when there is no cerium ions, is in practise, impossible, that step must proceed by means of intermediate product.

The initial stage of the oxidation process characteristic for non-saturated compounds may be regarded, in a most probable manner, as a formation of unstable complex of the acid with cerium (IV) ions, when, at the same time, the double bond between carbon atoms shatters (8).

So, the general scheme of the reaction can be introduced in a following way:



Changes of the reagent concentrations in respect to time can be described by equations:

$$\frac{-dc_{\text{Ce(IV)}}}{dt} = k_1 (A)(\text{Ce(IV)}) + k_3 (\text{HA})(\text{Ce(IV)})$$

$$\frac{-dc_A}{dt} = k_1 (A)(\text{Ce(IV)})$$

$$\frac{-dc_{\text{HC}}}{dt} = k_2 (\text{HC}) - k_{-2} (\text{HA}) - k_1 (A)(\text{Ce(IV)})$$

$$\frac{-dc_{HA}}{dt} = k_3 (HA)(Ce(IV)) + k_{-2}(HA) - k_2 (HC)$$

With the assumption $k_3 \gg k_2$ $\frac{dc_{HA}}{dt} = 0$

$$\text{and } (HA) = \frac{k_2(HC)}{k_3 (Ce(IV)) + k_{-2}}$$

Thus, equation describing the change of cerium ions in respect to time will take a form:

$$\frac{-dc_{Ce(IV)}}{dt} = k_1(A)(Ce(IV)) + k_2(HC) \left\{ \frac{k_3 (Ce(IV))}{k_3(Ce(IV)) + k_{-2}} \right\}$$

Taking into account the above scheme of the reaction and also obvious assumptions ($k_3 \gg k_{-2}$) one is in position to write the final equation describing the changes of cerium (IV) ions concentration:

$$\frac{-dc_{Ce(IV)}}{dt} = k_1 (A)(Ce(IV)) + k_2 (HC) \quad (1)$$

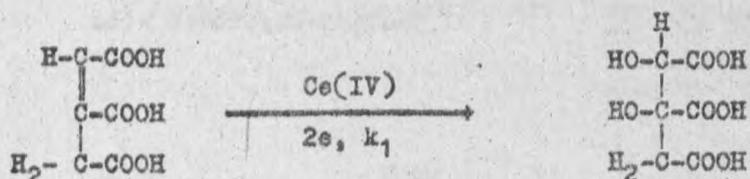
At the step I the concentration of intermediate product is, in practise, equal 0, probably the process proceeds through the stage of unstable complex: acetic acid-Ce(IV), where the excess of concentration of acid or cerium (IV) ions does not influence on complex concentration. Therefore, it is easy to explain the first order of the process at the step I. In the course of reaction the concentration of intermediate product increases, so the second term of equation (1) is responsible for its rate. When the value of rate constant of step II is greater ($k_2 > k_1$) (cis-acetic acid) then one can observe on experimental curves an appearance of characteristic collapses with greater slope (fig. 5, table 2).

In a similar way, the ordering of the process and run of kinetics curves can be explained in the case of trans-acetic acid. The characteristic collapses on curves $\lg c_{ac}$ is a function of time with excess concentration of cerium (IV) ions which have a smaller slope may be regarded most likely, as a

result of a smaller value of rate constant of II step ($k_2 < k_1$).

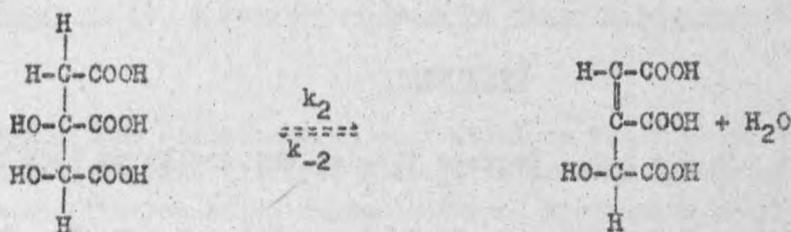
The step II undergoing without participation of cerium (IV) ions is probably the dehydration of intermediate product with formation of derivative non-saturated acid which is particularly susceptible on attack of oxidizer.

In conclusion, the initial stages of oxidation process of these two acids may be introduced in a following form:



cis-aconitic acid

3-hydroxycitric acid

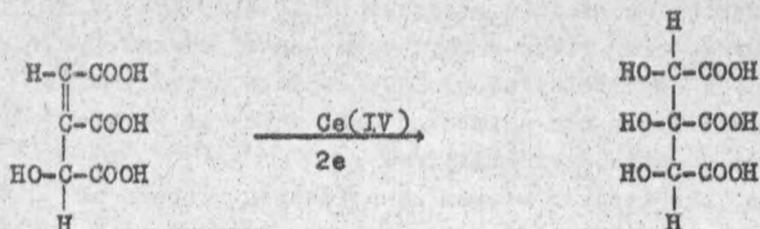


3-hydroxyaconitic acid

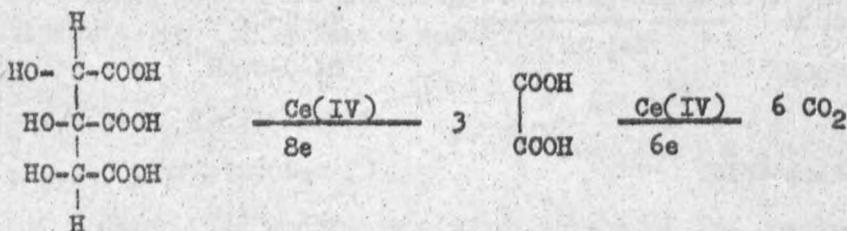
Differences in the rates of step II for cis- and trans-aconitic acid may be explained by the run of equilibrium reaction of dehydration of the trans-acid due to its spatial structure.

As the next stage of the oxidation process will be the shattering of double bond in 3-hydroxyaconitic acid and transformation of 1,3-dihydroxycitric acid.

The stoichiometry and the occurrence of CO_2 as the only one product of the reaction determine the form of the next steps, particularly the shattering of C-C bonds in 8-electron formation which forms 3 molecules of oxalic acid being oxidized quickly to a carbon dioxide.



1,3-dihydroxycitric acid

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Sabina Cieplak - Department of the
Science of Commodi-
ties, Economic Aca-
demy of Katowice

Maksymilian Ignaczak, Andrzej Grzejdziaik - Depart-
ment of the General
and Inorganic Che-
mistry, University
of Łódź

S.Cieplak, M.Ignaczak i A.Grzejdziaik

REAKCJE UTLENIANIA KWASÓW CIS- I TRANS-AKONITOWYCH
JONAMI Ce(IV) W WODNYCH ROZTWORACH KWASU NADCHLOROWEGO

Wyznaczono stechiometrię oraz ustalono produkty reakcji utlenienia. Zbadano kinetykę reakcji utleniania kwasów cis- i trans-akonitowych nadchloranem cerowym. Wyznaczono przy pomocy metody Ostwalda cząstkowe rzędy reakcji. Wykazano, iż przebiega ona w dwóch stadiach limitujących szybkość utleniania, przy czym jedno ze stadiów jest przemianą zachodzącą bez udziału jonów cerowych.

Wyznaczono również energię aktywacji etapów reakcji. Zaproponowano najbardziej prawdopodobny mechanizm procesu.