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THE DETERMINATION OF KINETIC PARAMETERS FOR THE REACTIONS OF OXIDATION OF ORGANIC COMPOUNDS BY CERIUM PERCHLORATE

THE NUMERICAL STUDY (PART III**)

The present paper is a continuation of earlier works concerning the method of determination of kinetic parameters for the oxidation reactions of organic compounds by cerium perchlorate in a solution of perchloric acid.

This paper deals with the case of oxidation of organic acids containing the -C=C- bond and describes the influence of perchloric acid on the reaction rate of oxidation at the compounds being regarded as a base according to the Brönsted theory.

During the oxidation of acids: fumaric [1], maleinic [2] and acrylic one [3] by the use of Cerium perchlorate one can observe, in practise, the zero - th reaction order in regard to reductor, while the reaction order in respect to the oxidizer is equal 1 [4].

The investigations upon the oxidation reactions of saturated, aliphatic carboxylic acids have shown, that the process of oxidation of these compounds does not occur, however, there are formed relatively stable complexes.

So, one may conclude that during the oxidation of carboxylic acids containing the C=C bond that process is realized by the decay of π - electron complexes being formed with the electrons of the C=C double bond.

That process can be introduced as it follows:

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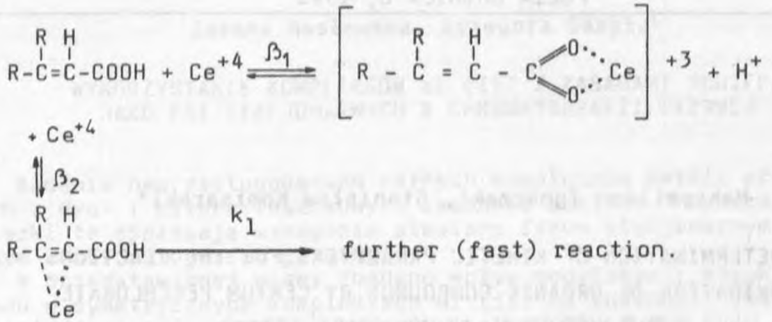
** Part I - Kinetika and Kataliz, XXV, 788-793 (1984); Part II - Kinetika AND Kataliz (in press).



Assuming an excess of oxidizer, the system of equations has the form:

$$-\frac{d\,Ce^{+4}}{dt} = n \cdot K_1 \cdot \left[\text{complex II}\right] \qquad (1)$$

$$\beta_1 = \frac{\left[\text{complex I}\right]}{C_{tCe^{+4}} \cdot C_{tR}} \qquad \beta_1 = \frac{\left[\text{complex I}\right] . H^{+}}{C_{tCe^{+4}} . C_{tR}} \qquad (2)$$

$$\beta_2 = \frac{\left[\text{complex II}\right]}{C_{tCe^{+4}} \cdot C_{tR}} \qquad (3)$$

$$C_{oR} - \frac{C_{oCe^{+4}} - C_{tCe^{+4}}}{n} = \left[\text{complex I}\right] + \left[\text{complex II}\right] + C_{tR} \qquad (4)$$

where:

$C_{tCe^{+4}}$ - Ce^{+4} concentration in time t,

C_{tR} - concentration of the free reductor in time t,

$C_{oCe^{+4}}$ - initial concentration of oxidizer,

C_{oR} - initial concentration of reductor,

n - electronicity of the process.

If the concentration of perchloric acid was constant during the measurement of reaction rate, one can take into account only the conditional stability constant of the complex I(β_1). Therefore, in order to obtain the K_1, β_1, β_2 parameters it is necessary to make the following transformations: dividing equation (2) by the equation (3) we get:

$$\frac{\beta_1}{\beta_2} = \frac{[\text{complex I}]}{[\text{complex II}]} \tag{5}$$

Determining from equs. (4) and (5) the value complex II we get:

$$[\text{complex II}] = \frac{C_{oR} - \frac{C_{oCe^{+4}} - C_{tCe^{+4}}}{n} - C_{tR}}{\frac{\beta_1}{\beta_2} + 1}$$

becouse $C_{tR} = \frac{[\text{complex II}]}{C_{tCe^{+4}} \cdot \beta_2}$

hence, we have:

$$[\text{complex II}] = \frac{C_{oR} - \frac{C_{oCe^{+4}} - C_{tCe^{+4}}}{n}}{\frac{\beta_1}{\beta_2} + 1 + \frac{1}{C_{tCe^{+4}}\,(\beta_1 + \beta_2)}}$$

the final equation is as it follows

$$\frac{-\,d\,Ce^{+4}}{dt} = n \,.\, K_1 \frac{C_{oR} - \frac{C_{oCe^{+4}} - C_{tCe^{+4}}}{n}}{\frac{\beta_1}{\beta_2} + 1 + \frac{1}{C_{tCe^{+4}}\,(\beta_1 + \beta_2)}} \tag{6}$$

The K_1, β_1, β_2 in equation (6) we determine by means of the nonlinear least squares method (the same as the determining the first derivative of Ce^{+4} concentration in respect to time). In the case of the dependence of reaction rate upon the perchloric acid concentration the sufficient condition is that $\beta_1 = \beta_1^*/H^+$. During the oxidation of non - saturated carboxylic acids the reaction order equal to I is characteristic.

The most often met oxidation reactions of organic compounds are that ones, in which, the dependence of reaction rate upon the perchloric acid concentration is very small, for example the oxidation of: ethylene alcohol and glicerine [5], propanole and isopropanole [6] butanedioles and butene-2-diol-1, 4 [7].

The double increase of acid concentration in the range 0.5--5 mole/cm^3 causes the increase of reaction rate from 5% up to 35%. This fact is due to the partial hydrolysis of Ce^{+4} ions and also it is caused by the change of activity coefficients in very concentrated electrolyte [8], [9]. Also, there are known the processes, in which, the increase of perchloric acid concentration causes rather significant lowering of reaction rate (about half in the case of the double increase of acid concentration). See the oxidation of hydroxypiridine [10] and of picolines, lutidines [11].

That mechanism can be made elear after the necessary assumption that the complex is formed between the nonprotonated amine and Cerium (IV) ion, according to the following scheme:

$$[\text{Amine} - H^+] \overset{K}{\rightleftharpoons} \text{Amine} + H^+$$

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

$$\text{complex} \xrightarrow{K_1} R + Ce^{+3} + H^+$$

$$R + (n-1)\,Ce^{+4} + (xH_2O) \xrightarrow{\text{fast}} \text{final products}$$

Because, the values of K for that amines are known or easy for determination by the potencjometric method (for the amines mentioned above the values of K are in $(10^{-5}, 10^{-3})$ interval) we propose the method of determination only the values K_1 and β.

The system of equations with an assumption of an excess of oxidizer has the form:

$$-\frac{d\,Ce^{+4}}{dt} = K_1 \cdot n\,[\text{complex}] \tag{7}$$

$$\beta = \frac{[\text{complex}]}{\text{Amine } C_{tCe^{+4}}} \tag{8}$$

$$C_{oA} - \frac{C_{oCe^{+4}} - C_{tCe^{+4}}}{n} = [\text{Amine}] + [\text{complex}] + [\text{Amine} - H^{+}] \tag{9}$$

$$K = \frac{[\text{Amine}]\ [H^{+}]}{[\text{Amine } H^{+}]} \tag{10}$$

where: C_{oA} - initial reductor concentration.

That system can be transformed in a following way: from equation (10) we determine $[\text{Amine} - H^{+}]$ and substitute this in equation (9).

Therefore, we get:

$$C_{oA} - \frac{C_{oCe^{+4}} - C_{tCe^{+4}}}{n} = [\text{Amine}]\ (1 + \frac{[H^{+}]}{K}) + [\text{complex}]$$

Making use of equation (8) we obtain:

$$C_{oA} - \frac{C_{oCe^{+4}} - C_{tCe^{-4}}}{n} = [\text{complex}] \left(\frac{1 + \frac{[H^{+}]}{K}}{.\ \beta\ .\ C_{tCe^{+4}}} + 1 \right)$$

and the final form of the equation is:

$$- \frac{d\ Ce^{+4}}{dt} = K_{1}\ .\ n\ \frac{C_{oA} - \dfrac{C_{oCe^{+4}} - C_{tCe^{+4}}}{n}}{\dfrac{1 + \frac{[H^{+}]}{K}}{\beta\ .\ C_{tCe^{+4}}} + 1} \tag{11}$$

The K_{1}, β parameters can be determined by means of the least squares method or using the approximate methods being described in details in paper [12]. It is also possible to determine the K constant if one will make use of a three - parameter equation, however, in that case one must perform the measurements of a high accuraccy (2%) which is rather difficult in a kinetics investigations. If the value of K is missed in calculations the determination of β leads a big error, however, the obtained K_1 value may be regarded as a good approximation.

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WYZNACZANIE PARAMETRÓW KINETYCZNYCH REAKCJI UTLENIANIA ZWIĄZKÓW ORGANICZNYCH NADCHLORANEM CEROWYM ZA POMOCĄ ETO (III)

Niniejsza praca jest kontynuacją wcześniej przedstawionych prac dotyczących metodyki wyznaczania parametrów kinetycznych reakcji utleniania związków organicznych nadchloranem cerowym w środowisku kwasu nadchlorowego.

Przedstawia ona metodykę ich wyznaczania w przypadku utleniania kwasów organicznych zawierających wiązanie -C=C- oraz opisuje wpływ kwasu nadchlorowego na szybkość reakcji utleniania związków, będących zasadami zgodnie z teorią Brönsteda.