

Kinetics and mechanism of the oxidation of acrolein, crotonaldehyde, and methacrolein with cerium(IV) sulfate

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The kinetics and mechanism of the oxidation of acrolein, crotonaldehyde, and methacrolein with cerium(IV) sulfate in a sulfuric acid solution have been studied. In the presence of adequate excess of acrolein or methacrolein, the reaction is of the zero order with respect to concentration of the Ce(IV) ions. As for crotonaldehyde, the reaction is of the first order with respect to the Ce(IV) ions as well as to substrate. In any case, the reaction is acid-catalyzed and the reaction rate decreases with increasing concentration of the HSO_4^- ions.

On the basis of experimental results, a reaction mechanism has been proposed according to which the slow and rate-determining step in the oxidation of acrolein and methacrolein is an acid-catalyzed hydration of aldehyde.

Была изучена кинетика и механизм окисления акролеина, кротонового альдегида и метакролеина сульфатом церия(IV) в растворе серной кислоты. При достаточно высоком избытке акролеина или метакролеина реакция обладает нулевым порядком по отношению к концентрации ионов Ce(IV). В случае кротонового альдегида реакция является реакцией первого порядка по отношению к ионам Ce(IV) и также к субстрату. Во всех случаях реакция протекает по кислотному катализу и скорость реакции уменьшается с повышением концентрации ионов HSO_4^- .

На основании экспериментальных данных был предложен механизм реакции, по которому контролирующей стадией окисления акролеина и метакролеина является кислотно катализуемая гидратация альдегида.

The oxidation of organic compounds with the Ce(IV) ions was synoptically described by Richardson [1]. As for aldehydes, the kinetics and oxidation mechanism of formaldehyde [2—8], acetaldehyde [9, 10], propionaldehyde [10], and benzaldehyde [11] in different media were studied. The analysis of kinetic results has shown that the oxidation of formaldehyde with the Ce(IV) ions proceeds in two successive one-electron steps. The hydrated formaldehyde is oxidized in the first step by a Ce(IV) ion to give a radical which is oxidized in the

second step by other Ce(IV) ion to yield formic acid. According to [4, 5] and [8], both steps are preceded by the formation of an intermediary complex in the ratio 1 : 1. According to *Sankhla* and *Mehrotra* [5, 6], the oxidation in sulfuric acid solution obeys an inner-sphere mechanism through the $\text{Ce}(\text{SO}_4)_2\text{—HCHO}$ complex while the oxidation in perchloric acid solution follows an outer-sphere mechanism.

The oxidation kinetics of other aldehydes with the Ce(IV) ions has been only incompletely investigated. The oxidation of unsaturated aldehydes with the Ce(IV) ions has not been yet investigated in more detail and for this reason, it is the topic of this paper which is the continuation of our studies dealing with the oxidation with the Tl(III) ions [12, 13].

Experimental

Kinetics

The kinetics of the oxidation of acrolein, crotonaldehyde, and methacrolein with cerium(IV) sulfate in aqueous sulfuric acid solution was studied polarographically and spectrophotometrically. The polarographic investigation was based on recording of the time dependence of limiting diffusion current of the cathodic wave of the Ce(IV) ions at the potential of 0 V against the potential of 1 M mercurousulfate electrode. The vibration platinum electrode of the frequency of 50 Hz (length 12 mm, width 0.5 mm) was used as an indication electrode. The measurements were carried out with a polarograph OH 102 (Radelkis, Budapest). The temperature-controlled Kalousek vessel was used as an electrolytic vessel. The spectrophotometric measurements were performed on a spectrophotometer Specord UV VIS (Zeiss, Jena) which was equipped with a thermostat block joint to an external thermostat. The temperature was held at a constant value by means of a thermostat U 10 (Medingen, Dresden) ($\pm 0.05^\circ\text{C}$).

Chemicals

Acrolein (pure, Fluka AG, Buchs SG) was distilled in a Vigreux column in nitrogen atmosphere. The fraction of boiling point $51.5\text{—}52.5^\circ\text{C}$ was taken as sample. Crotonaldehyde (pure, Fluka AG, Buchs SG) was distilled in a Vigreux column in nitrogen atmosphere. The fraction of boiling point $104\text{—}105^\circ\text{C}$ was taken as sample. Methacrolein (pure, Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague) was distilled in a Vigreux column in nitrogen atmosphere. The fraction of boiling point $68\text{—}69^\circ\text{C}$ was taken as sample. The substances were held in nitrogen atmosphere in a refrigerator [14]. The preparation of solutions of acrolein, crotonaldehyde, and methacrolein and their manipulation as well as measurements were performed in nitrogen atmosphere. No solution older than 24 h after distillation was used for measurement. Cerium(IV) sulfate (anal. grade, VEB Laborchemie) and other chemicals and solvents used were anal.

grade chemicals. Redistilled water was used for the preparation of all solutions. The reaction stoichiometry was determined by polarometric titration.

Analysis of reaction products

On completion of the reaction of acrolein with the Ce(IV) ions in aqueous sulfuric acid solution, the saturated solution of 2,4-dinitrophenylhydrazine in 2 M hydrochloric acid was added. The mixture was allowed to stand for three days at room temperature. The separated yellow-brown precipitate was filtered, dried and dissolved in benzene. The benzene solution was concentrated. The thin-layer chromatography on Silufol (UV 254, Kavalier, Votice) providing distinctly visible individual spots was applied to identifying the products. Benzene was used as an eluent.

The absence of acrylic acid was proved by capillary isotachopheresis. Moreover, it was evidenced by isotachopheresis that formic acid was formed in the presence of excess Ce(IV) ions in the reaction mixture. The instrument used is described in [15]. It enabled us to make analysis without any foregoing treatment [12]. The leading electrolyte was 10^{-2} M hydrochloric acid titrated to pH 3.7 with β alanine. 10^{-3} M caproic acid was used as terminating electrolyte. The detection limit for the investigated set of substances (dosing 8 μ l of solution) made possible identification and determination of acids the concentration of which in the reaction mixture was 10^{-5} M and higher. It was ascertained by quantitative analysis that the reaction mixture contained formic acid in 2×10^{-4} M concentration when the initial concentrations of reactants were: 10^{-3} M-Ce(SO₄)₂ and 2×10^{-4} M acrolein in 0.2 M-H₂SO₄.

Results

The oxidation of crotonaldehyde with the Ce(IV) ions in 0.2 M sulfuric acid solution is a first-order reaction with respect to the Ce(IV) ions as well as to substrate (Table 1). The slope of the linear dependence of the rate constant k_{exp} on crotonaldehyde concentration gives the value of rate constant at 17.5°C $k' = 6.5 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Table 1

Variation of experimental rate constant with concentration of crotonaldehyde
 10^{-3} M-Ce(SO₄)₂, 0.2 M-H₂SO₄, $t = 17.5^\circ\text{C}$

Concentration of crotonaldehyde $c \cdot 10^2/\text{M}$	Experimental rate constant $k_{\text{exp}} \cdot 10^2/\text{s}^{-1}$	Rate constant $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1.5	0.91	0.65
2.5	1.51	
3.5	1.98	
4.5	2.64	
5.5	3.60	
6.5	4.05	

Table 2

Variation of rate constant with concentration of substrate
 10^{-3} M-Ce(SO₄)₂, 0.2 M-H₂SO₄, $t = 17.5^{\circ}\text{C}$

Concentration of substrate $c \cdot 10^2/\text{M}$	Rate constant $k \cdot 10^4/\text{s}^{-1}$ of the oxidation	
	Acrolein	Methacrolein
1.5		
2.5		
3.5	8.3	0.89
4.5		
5.5		

For the oxidation of acrolein and methacrolein, the reaction is of the zero order with respect to the Ce(IV) ions provided the substrate is present in sufficient excess. The measured reaction rate is a linear function of concentration of the substrate. The rate constant evaluated from the slope of this relationship is $k = 8.3 \times 10^{-4} \text{ s}^{-1}$ for acrolein and $k = 8.9 \times 10^{-5} \text{ s}^{-1}$ for methacrolein at 17.5°C (Table 2). For stoichiometric ratio of both reactants ($[\text{Ce(IV)}] : [\text{S}] = 2$), the reduction of the Ce(IV) ions by acrolein or methacrolein is governed by the following rate equation

$$-\frac{d[\text{Ce(IV)}]}{dt} = k^n [\text{Ce(IV)}]^n \quad (1)$$

where $n = 1.3-1.4$.

We investigated the influence of temperature on the value of rate constant for all three reactions (Table 3) and calculated the corresponding values of activation enthalpies and activation entropies from the Eyring equation by using the least-square method (Table 4).

Table 3

Dependence of rate constant on temperature
 10^{-3} M-Ce(SO₄)₂, 0.2 M-H₂SO₄

$t/^{\circ}\text{C}$	A $k \cdot 10^3/\text{s}^{-1}$	K $k/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	M $k \cdot 10^4/\text{s}^{-1}$
10	0.44	—	—
17.5	0.83	0.65	0.89
25	1.44	0.92	1.32
30	2.01	1.25	1.68
35	—	1.59	2.17

A — acrolein, K — crotonaldehyde, M — methacrolein.

Table 4

Activation parameters of the oxidation of acrolein (A),
crotonaldehyde (K), and methacrolein (M) with cerium(IV) sulfate
 10^{-3} M-Ce(SO₄)₂, 0.2 M-H₂SO₄

Substrate	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J K ⁻¹ mol ⁻¹	ΔG^\ddagger kJ mol ⁻¹
A	51.2	-128	88.3
K	35.1	-127	72.2
M	35.2	-201	93.7

Table 5

Values of rate constants and catalytic constants
 10^{-3} M-Ce(SO₄)₂, 1.5×10^{-2} M-A, K, M, $I = 0.6$ M, $t = 17.5^\circ\text{C}$,
 I adjusted with NaHSO₄

Rate and catalytic constants	A	K	M
$k_0 \cdot 10^4/\text{s}^{-1}$	5.5	61	0.45
$k_{\text{H}_3\text{O}^+} \cdot 10^3/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.2	5.1	0.19

A — acrolein, K — crotonaldehyde, M — methacrolein.

The rate constant is a linear function of concentration of the H₃O⁺ ions in accordance with the generalized relationship

$$k = k_0 + k_{\text{H}_3\text{O}^+}[\text{H}_3\text{O}^+] \quad (2)$$

We evaluated the corresponding rate constants k_0 and $k_{\text{H}_3\text{O}^+}$ by the least-square method (Table 5).

As evident from Fig. 1, the value of rate constant decreases nonlinearly with increasing concentration of the HSO₄⁻ ions at constant concentration of the H₃O⁺ ions and constant ionic strength. Besides, for the oxidation of acrolein and methacrolein with the Ce(IV) ions, the reaction order with respect to the Ce(IV) ions changes with increasing concentration of the HSO₄⁻ ions from the value $n = 0$ to the value $n = 1$. An addition of the Ce(III) ions does not affect the reaction rate.

The value of rate constant decreases linearly with square root of ionic strength. By using the Bjerrum—Brönsted equation, we determined the values of the slope $z_A z_B = -0.57$ for crotonaldehyde and $z_A z_B = -0.28$ for acrolein as well as methacrolein.

The kinetics of the above redox reactions may be also investigated spectrophotometrically in the u.v. region on the basis of the decrease in absorbance of the Ce(IV) ions at $\lambda_{\text{max}} = 320$ nm. The original absorption maximum of the Ce(IV)

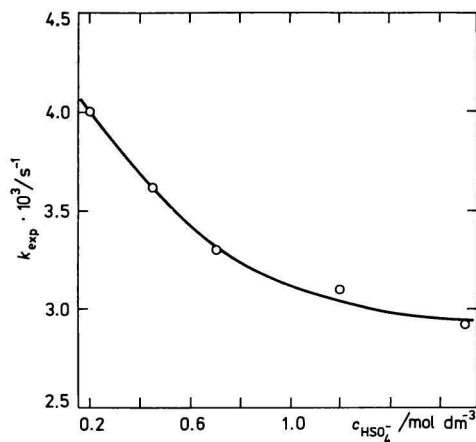


Fig. 1. Experimental rate constant of the redox reaction of the Ce(IV) ions with crotonaldehyde (K) as a function of concentration of the HSO_4^- ions.

$3.5 \times 10^{-4} \text{ M-Ce}(\text{SO}_4)_2$; $1.5 \times 10^{-2} \text{ M-K}$; $\text{H}_3\text{O}^+ = 0.2 \text{ M}$;
 $I = 1.7 \text{ M}$; $t = 17.5^\circ\text{C}$; I adjusted with NaClO_4 .

ions as well as the value of half-wave potential ($E_{1/2} = +0.25 \text{ V}$ against the 1 M mercurousulfate electrode) is not shifted in the presence of substrates. Similarly, the absorption maxima of the hydrated substrates ($\lambda_{\text{max}} = 212 \text{ nm}$ for acrolein, $\lambda_{\text{max}} = 224 \text{ nm}$ for crotonaldehyde, and $\lambda_{\text{max}} = 221 \text{ nm}$ for methacrolein) are also not shifted.

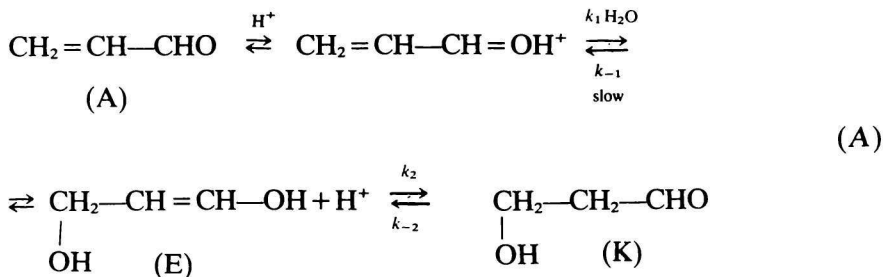
The stoichiometry determined by polarometric titration indicates the consumption of two Ce(IV) ions for a molecule of substrate. The analysis of the reaction mixture by the use of isotachopheresis in the presence of excess Ce(IV) ions reveals the formation of formic acid. Furthermore, it has been ascertained by isotachopheresis that acrylic acid does not occur in the reaction mixture. Besides, the analysis by thin-layer chromatography indicates the formation of three carbonyl compounds.

Discussion

If we compare the values of the Gibbs activation energies of all three aldehydes, we obtain the following order: $\Delta G^\ddagger = 72.2 \text{ kJ mol}^{-1}$ for crotonaldehyde, $\Delta G^\ddagger = 88.3 \text{ kJ mol}^{-1}$ for acrolein, and $\Delta G^\ddagger = 93.7 \text{ kJ mol}^{-1}$ for methacrolein at 17.5°C . This order in reactivity was also observed in the oxidation of the above substrates with the Tl(III) ions [12, 13] as well as in their oxidation with the Mn(III) ions [16].

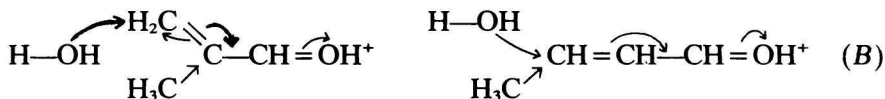
In harmony with the conclusions of papers [12, 13, 16], the following reaction mechanism may be assumed in this case. The proper redox step must be evidently

preceded by an acid-catalyzed hydration according to the following scheme which is the slow and rate-determining step of the overall reaction if that is a zero-order reaction with respect to the Ce(IV) ions



A relatively low value of the slope for primary salt effect is in harmony with the above idea. Such influence of ionic strength hints at the ion-dipole interaction which could correspond to hydration of the proton substrate in the rate-determining step.

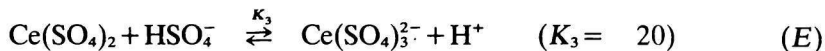
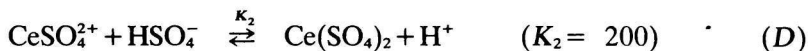
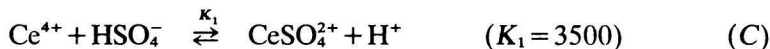
This order in reactivity of aldehydes may be explained as follows



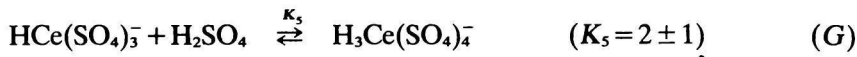
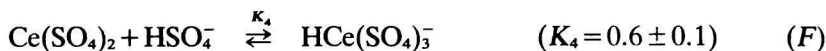
According to this scheme, the + I effect of the methyl group on the α carbon atom hinders the catalyzed hydration of the double bond owing to partial compensation of the mesomeric effect of the carbonyl group. On the other hand, the methyl group in the β position increases polarization of the double bond owing to + I effect. The relatively fastest hydration of crotonaldehyde results in the fact that the proper redox reaction with the Ce(IV) ions is under given conditions a first-order reaction with respect to oxidant. In this case, the catalyzed hydration does not more determine the rate of the proper redox step.

As the value of λ_{\max} as well as $E_{1/2}$ of the Ce(IV) ions does not shift in the presence of substrates, no conclusive evidence of the formation of an intermediary complex exists. Though the expected inner-sphere mechanism could not be proved in this way, its existence is not out of the question.

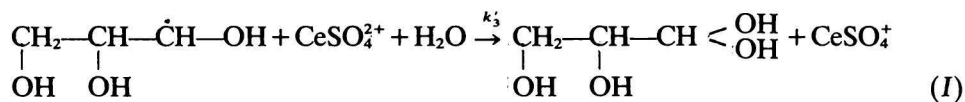
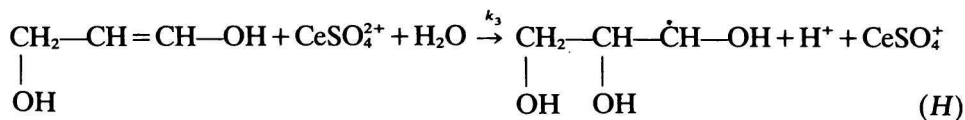
It results from the dependence of rate constant on concentration of the HSO_4^- ions that we may assume a shift in consecutive equilibrium of the Ce(IV) complexes in favour of species with a higher number of coordinated sulfate ions. According to *Hardwick and Robertson* [17], the following equilibria come into consideration



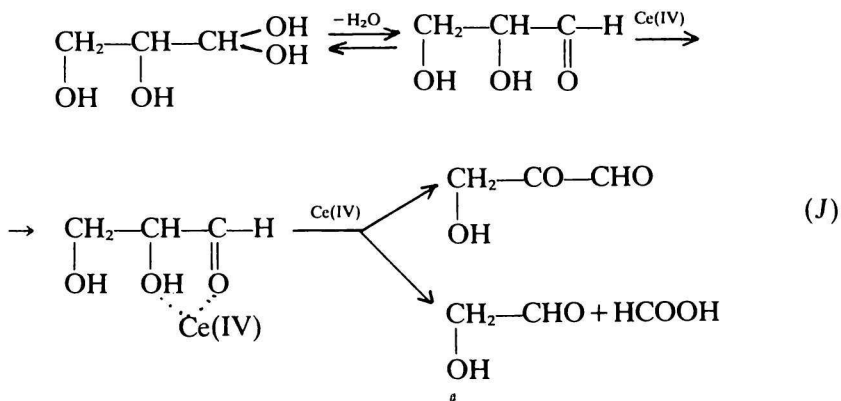
Bugaenko and Kuan-Lin [18] determined other equilibria in 0.1—17.6 M solutions of H_2SO_4 at 20°C



Because of character of the dependence of rate constant on ionic strength and concentration of the HSO_4^- ions, it is very likely that the CeSO_4^{2+} ion is the reactive particle. The equilibrium concentration of the CeSO_4^{2+} ions as well as the reaction rate decreases with increasing concentration of the HSO_4^- ions. The CeSO_4^{2+} ion attacks the double bond of the enol form according to the scheme



For instance, if acrolein reacts with the $\text{Ce}(\text{IV})$ ions in stoichiometric ratio, the main product of oxidation is glyceraldehyde. In the presence of excess $\text{Ce}(\text{IV})$ ions, the oxidation continues according to the following scheme [19], the rate constant being $k = 3.5 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$



Formic acid was proved in the reaction mixture by capillary isotachopheresis.

Since step (I) is much faster than step (H), the rate equation assumes the form

$$-\frac{d[\text{CeSO}_4^{2+}]}{dt} = k_3[\text{CeSO}_4^{2+}][\text{E}] \quad (3)$$

where [E] is the steady-state concentration of the enol form present in major part of reaction path. It obeys the equation

$$\frac{d[\text{E}]}{dt} = k_1[\text{A}] - k_{-1}[\text{E}] - k_2[\text{E}] + k_{-2}[\text{K}] - k_3[\text{E}][\text{CeSO}_4^{2+}] = 0 \quad (4)$$

and hence

$$[\text{E}] = \frac{k_1[\text{A}] + k_{-2}[\text{K}]}{k_{-1} + k_2 + k_3[\text{CeSO}_4^{2+}]} \quad (5)$$

Thus, we obtain

$$-\frac{d[\text{CeSO}_4^{2+}]}{dt} = k_3[\text{CeSO}_4^{2+}] \frac{k_1[\text{A}] + k_{-2}[\text{K}]}{k_{-1} + k_2 + k_3[\text{CeSO}_4^{2+}]} \quad (6)$$

Since the proper redox step is rapid, it holds

$$k_3[\text{CeSO}_4^{2+}] \gg k_{-1} + k_2 \quad (7)$$

and

$$k_1[\text{A}] \ll k_{-2}[\text{K}] \quad (8)$$

and the rate equation assumes the form

$$-\frac{d[\text{CeSO}_4^{2+}]}{dt} = k_{-2}[\text{K}] \quad (9)$$

As the equilibria involving individual species of the Ce(IV) ions are mobile enough, it holds

$$-\frac{d[\text{Ce(IV)}]}{dt} = k[\text{K}] \quad (10)$$

which is in conformity with observation if acrolein or methacrolein is present in sufficient excess.

Provided the reverse inequality is valid

$$k_3[\text{CeSO}_4^{2+}] \ll k_{-1} + k_2 \quad (11)$$

we obtain

$$-\frac{d[\text{CeSO}_4^{2+}]}{dt} = k_{-2}k_3[\text{CeSO}_4^{2+}] \frac{[\text{K}]}{k_{-1} + k_2} \quad (12)$$

or

$$-\frac{d[\text{Ce(IV)}]}{dt} = k'[\text{Ce(IV)}][\text{K}] \quad (13)$$

which is to be observed in the oxidation of crotonaldehyde.

For the stoichiometric ratio of the Ce(IV) ions and acrolein or methacrolein, the condition of the steady state is not likely to be valid and thus the zero reaction order vanishes. Under these conditions, the concentration of the Ce(IV) ions decreases according to rate eqn (1) where $n = 1.3\text{--}1.4$.

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