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A KINETIC STUDY UPON THE OXIDATION OF BENZALDEHYDE BY CERIUM(IV) IN SULPHURIC ACID MEDIA

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ABSTRACT. The kinetics of benzaldehyde oxidation to benzoic acid by ceric sulphate has been studied using spectrophotometrical means, in a H_2SO_4 – Na_2SO_4 – $NaClO_4$ mixture. The influence of organic substrate, hydrogen ion and sulphate ion concentration as well as the effect of ionic strength upon the rate was investigated over a wide range. The kinetic study revealed the existence of two stages, each of first-order with respect to Cerium(IV). The first step involves the formation of an intermediate complex between Ce(IV) and benzaldehyde. The second step consists of the electron transfer within this 1:1 Ce(IV):benzaldehyde complex. The rate laws for both processes were found and a mechanism was suggested in accordance with the experimental results. The activation parameters for both processes were obtained.

INTRODUCTION

Cerium (IV) is a good oxidizing agent for a large number of organic substrates, because of the relative high oxidation potential of Ce(IV)/Ce(III) system [1]. Many oxidations of various classes of organic molecules are reported in the literature. For example we mention the oxidation of aromatic hydrocarbons [2-4], aliphatic [5-8] and aromatic alcohols [9-12], aldehydes [13-16], organic acids [17-18], phenols [19] etc by Ce(IV) in various acidic media. The Ce(IV)/Ce(III) redox system was also successfully employed as a mediator in the indirect anodic oxidation of toluene [20] and p-xylene [21].

An extended kinetic study on benzaldehyde oxidation by Ce(IV) [16], which was performed in acetic acid medium established the formation of some intermediate complexes between Ce(IV) and benzaldehyde. The authors found the rate law for the oxidation process and developed a mechanism that included besides the complex formation the decay of the complex by internal electron transfer yielding the benzoyl radical.

It is the purpose of this study to complete the investigation on the oxidation of toluene and benzyl alcohol by Ce(IV), undertaken in our laboratory, using sulphuric medium.

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EXPERIMENTAL

All the chemicals employed were of reagent grade purity and came from "Reactivul Bucureşti", "Carlo Erba-Milano" and "Merck". Stock solutions were prepared in twice distilled water. Reaction kinetics was followed spectrophotometrically on a Spekol-Zeiss spectrophotometer provided with a temperature jacket surrounding the cells. The jacket was connected to a Wobser U-10 thermostat which kept the temperature constant within $\pm 0{,}1^0$C. The reaction mixtures were prepared directly in a quartz cell with 5 cm path length and the absorbance was measured at 350 nm. The kinetic runs were started by adding a measured amount of Ce(IV) stock solution to the mixture containing benzaldehyde, H_2SO_4, Na_2SO_4, $NaClO_4$ and twice distilled water.

RESULTS AND DISCUSSIONS

Preliminary investigations

The solubility check. Benzaldehyde solubility was determined by spectrophotometrical means in a H_2SO_4 – Na_2SO_4 – $NaClO_4$ aqueous mixture, at 20 and 40^0C. The hydrogen ion concentration of the nine solutions varied from 0,15 to 0,65 mol/dm^3 at constant sulphate ion concentration (0,6 mol/dm^3) and constant ionic strength (1,5 mol/dm^3). They were saturated in benzaldehyde.The solubility limits varied within this range of acidity from $1{,}88\cdot10^{-3}$ to $4{,}44\cdot10^{-3}$ at 20^0C and from $3{,}1\cdot10^{-3}$ to $7\cdot10^{-3}$ mol/dm^3 at 40^0C.

Complex formation and check on Lambert Beer law validity. The formation of an 1:1 complex between Ce(IV) and benzaldehyde with the apparent equilibrium constant K_{app} = 375±7 dm^3/mol ($[H^+] = 0{,}7$; $[SO_4^{2-}] = 0{,}6$ and ionic strength, $\mu = 1{,}5$ mol/dm^3; t = 25^0C) was previously proved by recording the absorbance spectra of several benzaldehyde – Ce(IV) mixtures [22]. That approach did not make allowance of sulphate ion and hydrogen ion concentration. Taking into account the effect of these species on the complex formation a new value of 193±4 has been calculated from the equilibrium:

$$CeSO_4^{2+} + C_6H_5CH(OH)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} CeSO_4 \bullet OCH(OH)C_6H_5 + H^+ \quad (1)$$

Because Ce(IV) forms many sulphatocomplexes in sulphuric acid solution [23-24] and because kinetic measurements were performed by spectrophotometrical means, the validity of Lambert-Beer law needed to be checked over the range of Ce(IV), SO_4^{2-} and H^+ concentrations used in our experiments. We obtained linear A = f([Ce(IV)] plots in the absence as well as in the presence of benzaldehyde, at two wavelengths.

Table 1.

Molar absorbance coefficients for ceric sulphate at 25^0C.

Mixture	λ nm	E $dm^3 \cdot mol^{-1} \cdot cm^{-1}$
$2 \cdot 10^{-5} \leq [Ce(IV)] \leq 5 \cdot 10^{-5}$ mol/dm^3 $[H^+] = 0.7$ mol/dm^3 $[SO_4^{2-}] = 0.6$ mol/dm^3 $\mu = 1.5$ mol/dm^3	350 360	5000±26 4000±8
$2 \cdot 10^{-5} \leq [Ce(IV)] \leq 5 \cdot 10^{-5}$ mol/dm^3 $[H^+] = 0.7$ mol/dm^3 $[SO_4^{2-}] = 0.6$ mol/dm^3 $[C_6H_5CHO] = 10^{-4}$ mol/dm^3 $\mu = 1.5$ mol/dm^3	350 360	4580±50 3800±15

As shown in table 1 the molar absorptivities are smaller the presence of benzaldehyde, a fact that may be also considered as an evidence for the formation of an complex between Ce(IV) and benzaldehyde.

Kinetics

All kinetic runs were performed in the presence of benzaldehyde excess. Under such set of experimental conditions, the absorbance readings were processed according to the integrated form of a first order rate law:

$$\ln(A - A_\infty) = \ln(A_0 - A_\infty) - k_{obsd} \cdot t \qquad (2)$$

where: - A_0, A_∞ and A stand for the absorbance at the beginning, at the end of the process and at different time intervals, t, from the start of reaction, respectively;

- k_{obsd} is the observed first-order rate constant.

The semilogarithmic plots $\ln(A - A_\infty) = f(t)$, that were obtained for several excess concentrations of benzaldehyde, exhibited an initial curved part at small degrees of reaction, followed by a linear part up to around 90% of completion (Fig. 1)

This biphasic plots can be attributed to a reaction sequence consisting of two processes:

$$\text{Ce(IV)} + C_6H_5CHO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{Complex} \xrightarrow{k_2} \text{Ce(III)} + \text{Products} \qquad (3)$$

Under the excess concentration of benzaldehyde it simplifies to:

$$A \xrightarrow{k_{obsd1}} B \xrightarrow{k_{obsd2}} C \qquad (4)$$

where A stands for Ce(IV), B for the Ce(IV)-benzaldehyde complex and C for the product.

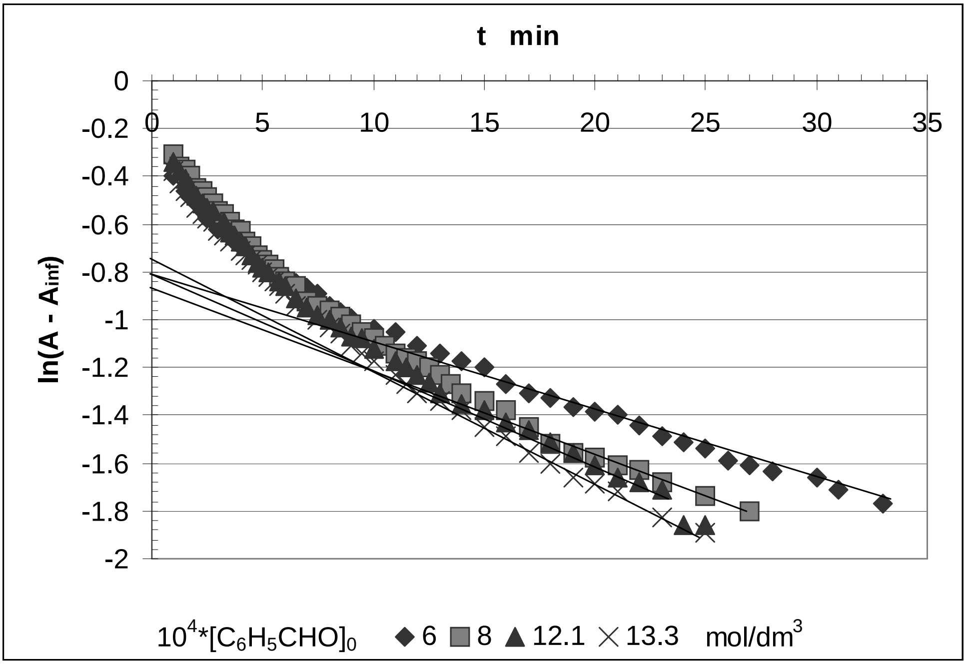

Figure.1. First-order plots for benzaldehyde oxidation with Ce(IV); [Ce(IV)]=$5\cdot10^{-5}$; [H^+]=0.6; [SO_4^{2-}]=0.6 and (μ = 1.5 mol/dm^3; t=34^0C

The first order rate constant for the complex formation process is $k_{obsd1} = k_1\cdot[C_6H_5CHO] + k_{-1}$ and the first order rate constant for the oxidation process is k_{obsd2}. In order to determine the rate constants for these two processes we employed a method that is further described.

The absorbance of the reaction mixture, at any moment, results from the contributions of all coloured species at 350 nm. In this case they are: the ceric sulphate, the complex and, with a rather very small contribution, the product.

$$A = \varepsilon_A\cdot d\cdot C_A + \varepsilon_B\cdot d\cdot C_B + \varepsilon_C\cdot d\cdot C_C \tag{5}$$

where A stands for the absorbance of the mixture, ε is the molar absorbance coefficient, C is the concentration and d stands for the cells path length. If C_A, C_B and C_C from relation (5) are replaced with the well known, time dependent equations of reactant, intermediate and product concentration for a first-order consecutive reaction, we obtain:

$$A - A_\infty = C_{A0} d\left[\varepsilon_A + \frac{k_{obsd2}\varepsilon_C - k_{obsd1}\varepsilon_B}{k_{obsd1} - k_{obsd2}}\right]\exp(-k_{obsd1}t) + C_{A0} d\,\frac{k_{obsd1}(\varepsilon_D - \varepsilon_C)}{k_{obsd1} - k_{obsd2}}\cdot \exp(-k_{obsd2}t) \tag{6}$$

where $A_\infty = \varepsilon_C\cdot C_{A0}$

Including all constant values into a preexponential factor, the equation (6) becomes:

$$A - A_\infty = \gamma_1 \exp(-k_{obsd1} t) + \gamma_2 \exp(-k_{obsd2} t) \qquad (7)$$

The semilogarithmic plot of ln(A - A_∞) vs t would be a curve that becomes a straight line at higher degrees of transformation. For long reaction times, provided that $k_{obsd1} > k_{obsd2}$, which is valid to our system, the term exp(k_{obsd1}·t) has a negligible contribution to the sum and:

$$\ln(A - A_\infty) = \ln\gamma_2 - k_{obsd2} \cdot t \qquad (8)$$

It allows to determine the constant γ_2 and the first-order rate constant k_{obsd2} from the intercept and slope of the line respectively.

At short reaction times, when the oxidation process is unimportant, the time dependent parameter Δ may be defined:

$$\Delta = A - A_\infty - \gamma_2 \exp(-k_{obsd2} \cdot t) = \gamma_1 \exp(-k_{obsd1} \cdot t) \qquad (9)$$

The slope of the line described by equation (8) and the linear form of (9) were obtained using a least square method. Two to four individual experiments were used for each set of conditions. First order dependence on [Ce(IV)] for complex formation and for its oxidation is proved by linear lnΔ = f(t) and ln(A - A_∞) = f(t) plots we obtained for all kinetic runs.

First-order rate constants calculated for both processes at several excess concentration of benzaldehyde are presented in table 2.

Table 2.

The dependence of first-order rate constants for complex formation and complex oxidation on the initial benzaldehyde concentration; [Ce(IV)]=$5\cdot10^{-5}$; [H^+]=0.6; [SO_4^{2-}]=0.6 and μ = 1.5 mol/dm^3; t=34^0C.

$10^4\cdot[C_6H_5CHO]_0$ mol/dm^3	$10^3 \cdot \overline{k_{obsd1}}$ s^{-1}	$10^4 \cdot \overline{k_{obsd2}}$ s^{-1}
6	3.9	5.8
8	4.8	6.6
10	5.6	7.1
12.1	6.3	7.4
13.3	6.7	7.7

The values of the first-order rate constants, for both processes increased with increasing benzaldehyde concentration according to:

$$k_{obsdi} = \frac{a_i \cdot [C_6H_5CHO]_0}{b_i + c_i \cdot [C_6H_5CHO]_0} \quad i = 1;2 \qquad (10)$$

with a trend to level off. A similar behaviour has been found in the case of glycolic acid oxidation. These findings indicate that the reaction order lies between zero and unity and that intermediate complex formation occurs [25].

Equation (10) may be transposed into the linear form:

$$\frac{1}{k_{obsdi}} = \frac{c_i}{a_i} + \frac{b_i}{a_i} \cdot \frac{1}{[C_6H_5CHO]_0} \qquad i = 1;2 \tag{11}$$

with: $c_1/a_1 = (59.2 \pm 0.1)$ s $\qquad c_2/a_2 = (918 \pm 62)$ s

$b_1/a_1 = (0.12 \pm 0.01)$ $s \cdot mol \cdot dm^{-3}$ $\qquad b_2/a_2 = (0.48 \pm 0.06)$ $s \cdot mol \cdot dm^{-3}$

From the intercept/slope ratio of the complex formation (eq.(11)) we obtained the apparent equilibrium constant K_{app} = (493 ± 3) dm^3/mol. Considering the effect of H^+ and SO_4^{2-} ions upon the reaction constant a value of 296 ± 8 has been calculated. There is a relative good agreement between this value of the apparent equilibrium constant (K_{app} = 493 dm^3/mol at 50^0C) and the equilibrium constant calculated from the absorbance spectra (K_{app} = 375 dm^3/mol at 25^0C) taking into account that these values were obtained at different values of temperatures,

To determine $[H^+]$ terms in the rate law we simply determined the first-order rate constant by varying the hydrogen ion concentration between 0.1 and 0.6 $mol \cdot dm^{-3}$ at constant concentration of benzaldehyde and sulphate. Table 3 assembles the rate data for four temperatures. Both the rate coefficients were affected by the hydrogen ion, suggesting the involvement of some acid-base equilibria.

As seen, the first stage first-order rate constant depends upon the hydrogen ion concentration by a linear equation:

$$k_{obsd1} = k_{01} + k_H \cdot [H^+] \tag{12}$$

On the basis of these findings we can conclude that a $[H^+]$ ion dependent and a linear dependent path contribute to the formation of the intermediate benzaldehyde-Ce(IV) complex.

Table 3.

The dependence of first-order rate constants for both stages on $[H^+]$; $[Ce(IV)] = 5 \cdot 10^{-5}$; $[C_6H_5CHO]_0 = 10^{-3}$; $[SO_4^{2-}] = 0.6$ and $\mu = 1.5$ mol/dm^3

	$[H^+]$ $mol \cdot dm^{-3}$						T K
	0.1	0.2	0.3	0.4	0.5	0.6	
$10^3 \cdot \overline{k_{obsd1}}$ s^{-1}	1.65	1.97	2.33	2.68	3.11	3.41	297
$10^5 \cdot \overline{k_{obsd2}}$ s^{-1}	3.72	10.2	13.9	18.6	21.5	25.7	
$10^3 \cdot \overline{k_{obsd1}}$ s^{-1}	3.15	3.51	4.24	4.39	5.11	5.58	307
$10^5 \cdot \overline{k_{obsd2}}$ s^{-1}	12.1	22.6	32.9	42.1	56.7	71.1	
$10^3 \cdot \overline{k_{obsd1}}$ s^{-1}	3.65	4.15	4.82	5.20	5.72	6.36	312
$10^5 \cdot \overline{k_{obsd2}}$ s^{-1}	21.3	40.9	62.9	78.3	99.6	113	
$10^3 \cdot \overline{k_{obsd1}}$ s^{-1}	4.49	4.87	5.66	6.33	7.00	7.84	321
$10^5 \cdot \overline{k_{obsd2}}$ s^{-1}	63.4	105	169	218	284	337	

On the other hand the second stage first-order rate constant shows only a linear dependence on [H^+], with a zero intercept, suggesting a catalytical process of the electron-transfer stage:

$$k_{obsd2} = k_2 \cdot [H^+] \qquad (13)$$

From the parameters of equation (12) and (13) we calculated the rate constant zero-order and first-order on the hydrogen ion concentration respectively. Data are summarized in table 4, along with the activation parameters calculated from them.

Table 5.

First-order and zero-order rate constants in [H^+], for both stages and the corresponding activation parameters; [Ce(IV)]=$5\cdot10^{-5}$; [C_6H_5CHO]$_0$ = 10^{-3}; [SO_4^{2-}]=0.6 and μ = 1.5 mol/dm^3

T K	Complex formation		Complex oxidation
	$10^3\cdot k_0$ s^{-1}	k_H dm$^3\cdot$mol$^{-1}\cdot$s^{-1}	$10^4\cdot k_2$ dm$^3\cdot$mol$^{-1}\cdot$s^{-1}
297	1.27	3.59	4.24
307	2.62	4.89	11.6
312	3.12	5.33	18.5
321	3.65	6.80	55.8
E_a kJ·mol^{-1}	35.2±5.0	20.9±2.0	84.6±4.0
ΔH^* kJ·mol^{-1}	32.4±5.0	18.3±2.0	82.1±4.0
ΔS^* J·mol^{-1}·K^{-1}	-190±14	-230± 10	-33.6±3.0

The activation parameters include the thermal and entropical effects of several preequilibria involved in the reaction mechanism.

On the contrary, sulphate ion exhibited an inhibitory effect on the rate, as shown in figure 2. An explanation for this behaviour consists on the expulsion of some sulphate ions from the first coordination sphere of Ce(IV) prior to the linkage of the benzaldehyde. The curves in figure 2 could be described by the equation:

$$k_{obsdi} = \frac{a_i}{b_i + c_i \cdot [SO_4^{2-}]^2} \qquad i = 1;2 \qquad (14)$$

which may be transposed into the linear form:

$$\frac{1}{k_{obsdi}} = \frac{b_i}{a_i} + \frac{c_i}{a_i} \cdot [SO_4^{2-}]^2 \qquad i = 1;2 \qquad (15)$$

with the parameters:

c_1/a_1 = (113 ± 10) dm^3·mol^{-1} s^{-1} c_2/a_2 = (2550 ± 200) dm^3·mol^{-1} s^{-1}
b_1/a_1 = (88 ± 4) s b_2/a_2 = (9.7 ± 1.3) s

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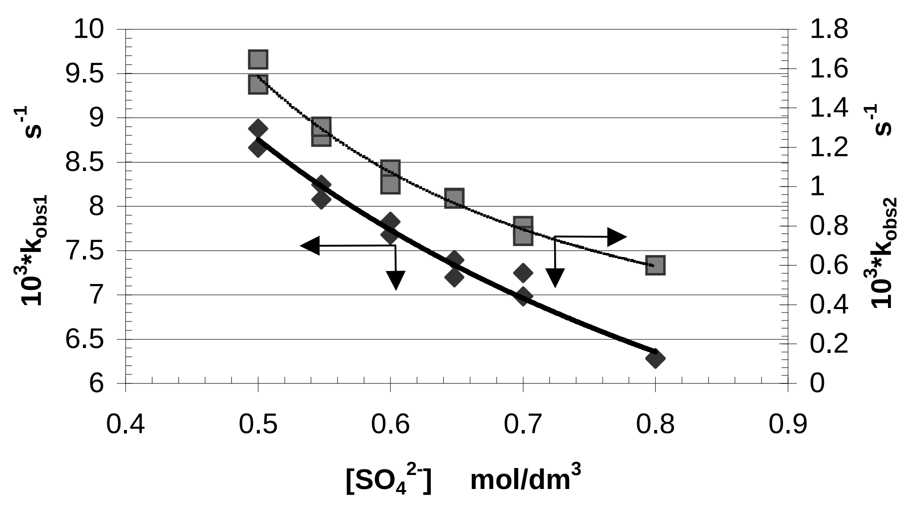

Figure 2. The influence of sulphate ion on the rate constants of complex formation, k_{obsd1}, and complex oxidation, k_{obsd2}; $[Ce(IV)]=5\cdot10^{-5}$; $[C_6H_5CHO]_0 = 10^{-3}$; $[H^+]=0,2$; $\mu=1,5$ mol/dm^3; t = 48^{0}C.

An increase of the ionic strength in the range of 0.73 to 1.76 mol/dm^3 at 48^{0}C, caused an increase of first order rate constants for both processes(table 4). The effect of ionic strength should be due to both primary and secondary salt effects. We found a linear dependence of same type for complex formation and for complex oxidation:

$$\ln k_{obsdi} = a_i + \frac{b_i \cdot \sqrt{\mu}}{1 + c_i \cdot \sqrt{\mu}} - d_i \cdot \mu \quad I = 1;2 \qquad (16)$$

Table 4.

The dependence of rate constants of complex formation and complex oxidation on the ionic strength; $[CE(IV)]=5\cdot10^{-5}$; $[C_6H_5CHO]_0 = 10^{-3}$; $[SO_4^{2-}]=0.6$ and $[H^+] = 0.2$ mol/dm^3; t = 48^{0}C

μ mol/dm^3	$10^3 \cdot \overline{k_{obsd1}}$ s^{-1}	$10^4 \cdot \overline{k_{obsd2}}$ s^{-1}
0.73	3.99	1.64
0.97	4.71	3.13
1.50	7.75	10.5
1.63	8.66	18.7
1.76	10.0	22.6

Considering the influence of the above mentioned factors like: cerium sulphate, benzaldehyde, hydrogen ion and sulphate ion concentration upon the reaction rate, we found the following experimental rate laws:

- for the process of complex formation:

$$r_1 = \frac{(\alpha_1 + \beta_1 \cdot [H^+]) \cdot [C_6H_5CHO]_0}{\gamma_1 \cdot [SO_4^{2-}]^2 + \delta_1 \cdot [C_6H_5CHO]_0} \cdot [Ce(IV)]_t \qquad (17)$$

- for the process of complex oxidation:

$$r_2 = \frac{\beta_2 \cdot [H^+] \cdot [C_6H_5CHO]_0}{\gamma_2 \cdot [SO_4^{2-}]^2 + \delta_2 \cdot [C_6H_5CHO]_0} \cdot [Ce(IV)]_t \qquad (18)$$

Mechanism

A reaction mechanism, considering the factors that exert an influence upon the reaction rates of the two processes as well as the negative values of their activation entropies, has been suggested.

As it was mentioned before cerium (IV) forms several sulphatocomplexes in sulphuric acid medium: $Ce(SO)_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$, $HCe(SO_4)_3^-$ etc. [23-24]. The species $Ce(SO_4)_3^{2-}$ prevails in the range of $[H^+]$ and $[SO_4^{2-}]$ in which we performed our measurements. But the inhibitory effect of sulphate ion indicates that the kinetic active species must be a ceric sulphatocomplex coordinated with less sulphate ions, like $CeSO_4^{2+}$. For its formation we considered the equilibrium:

$$Ce(SO_4)_3^{2-} + H^+ \rightleftarrows CeSO_4^{2+} + HSO_4^- + SO_4^{2-} \qquad K \quad (19)$$

The kinetic active species will react with the benzaldehyde in its hydrated form [26-30]:

$$C_6H_5CHO + H_2O \rightleftarrows C_6H_5CH(OH)_2 \qquad K_h \quad (20)$$

to yield the complex:

$$CeSO_4^{2+} + C_6H_5CH(OH)_2 \rightleftarrows CeSO_4{\cdot}OCH(OH)C_6H_5 + H^+ \qquad K_f = k_1/k_{-1} \quad (21)$$

The complex undergoes an internal electron transfer:

$$CeSO_4{\cdot}OCH(OH)C_6H_5 \longrightarrow C_6H_5CH(OH)O\bullet + Ce(III) \qquad k_2 \qquad (22)$$

The radical formed in this stage will be further oxidized by Ce(IV) to benzoic acid:

$$CeSO_4{\cdot}OCH(OH)C_6H_5 \longrightarrow C_6H_5CH(OH)O\bullet + Ce(III) \qquad k_2 \qquad (23)$$

Besides these steps we considered also the dissociation of HSO_4^-:

$$HSO_4^- \rightleftarrows SO_4^{2-} + H^+ \qquad K_a \qquad (24)$$

The concentration of $CeSO_4^{2+}$ from (19) is:

$$[CeSO_4^{2+}] = \frac{K \cdot [Ce(SO_4)_3^{2-}] \cdot [H^+]^2}{K_a \cdot [SO_4^{2-}]_t^2} \qquad (25)$$

where the total sulphate concentration is:

$$[SO_4^{2-}]_t = [SO_4^{2-}] + [HSO_4^{2-}] = [SO_4^{2-}]\cdot\left\{1+\frac{[H^+]}{K_a}\right\} \qquad (26)$$

Considering $K_a << [H^+]$, the sulphate concentration may be approximated by:

$$[SO_4^{2-}] \approx \frac{[SO_4^{2-}]_t\cdot K_a}{[H^+]} \qquad (27)$$

If only the contributions of $Ce(SO_4)_3^{2-}$ and the complex are considered, the mass balance for Ce(IV) is given by:

$$[Ce(IV)]_t = [Ce(SO_4)_3^{2-}] + [CeSO_4\cdot OCH(OH)C_6H_5] \qquad (28)$$

Employing the expression of complex concentration from its formation equilibrium (eq. 21) into the mass balance for Ce(IV), the concentration of the kinetic active species may be expressed as a function of total cerium sulphate concentration, $[Ce(IV)]_t$:

$$[CeSO_4^{2+}] = \frac{K\cdot[H^+]^2\cdot[Ce(IV)]_t}{K_a\cdot[SO_4^{2-}]_t^2 + K_f\cdot K\cdot K_h[H^+][C_6H_5CHO]_0} \qquad (29)$$

The rate law deduced for the formation of the Ce(IV)-benzaldehyde complex is:

$$r_1 = k_1\cdot K_h[CeSO_4^{2+}]\cdot[C_6H_5CHO] - k_{-1}\cdot[CeSO_4\cdot OCH(OH)C_6H_5]\cdot[H^+] \qquad (30)$$

or:

$$r_1 = \left(k_1\cdot[H^+]^2 - k_{-1}\cdot K_f\cdot[H^+]\right)\frac{K_h\cdot K\cdot[C_6H_5CHO]_0\cdot[Ce(IV)]_t}{K_a\cdot[SO_4^{2-}]_t^2 + K_f\cdot K\cdot K_h[H^+][C_6H_5CHO]_0} \qquad (31)$$

The rate law found for the oxidation process is:

$$r_2 = \frac{k_2\cdot K_f\cdot K_h\cdot[CeSO_4^{2+}]\cdot[C_6H_5CHO]_0}{[H^+]} \qquad (32)$$

or:

$$r_2 = \frac{k_2\cdot K_f\cdot K\cdot K_h\cdot[CeSO_4^{2+}]\cdot[H^+]\cdot[C_6H_5CHO]_0}{K_a\cdot[SO_4^{2-}]_t^2 + K_f\cdot K\cdot K_h[H^+][C_6H_5CHO]_0}\cdot[Ce(IV)]_t \qquad (33)$$

Both rate laws deduced from the suggested mechanism resemble to the experimental rate laws we found for the formation of the intermediate complex and its futher oxidation (eq. 17 and 18) and justifies the inhibition by sulphate. It gives support for this reaction scheme. Research are in progress in our laboratory and new data will illuminate these oxidations with cerium(IV).

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