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Kinetics and mechanism of silver(I) catalyzed oxidation of L-leucine by cerium (IV) in acid perchlorate medium

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ABSTRACT

The kinetics of the silver(I) catalyzed oxidation of Leucine with cerium(IV) has been studied in perchloric acid medium. A decrease in rate with increasing concentration of cerium(IV) is observed and the detailed quantitative analysis of this behaviour is presented on the basis of dimerization of cerium(IV). The reaction exhibits fractional dependence on Leucine and that has been accounted for the formation of an adduct with silver(I). A plausible reaction mechanism is given and the rate law is derived: $K = k_1K_1[Leu^+][H^+]/([H^+]+Kh)(1+K_1[Leu^+])$ (Where *k* is observed second order rate constant.)

KEYWORDS

Valine;
Cerium(IV);
Silver(I);
Perchloric acid.

INTRODUCTION

Amino acids play a significant role in a number of metabolic reactions. Specific metabolic roles of amino acids include the biosynthesis of polypeptides and proteins and the synthesis of nucleotides. Amino acids can undergo many types of reaction depending on whether a particular amino acids contains non-polar groups or polar substituents.The study of oxidation of amino acids is interesting as the oxidation products are different from different oxidants[1,2]. Thus the study of amino acids become important because of their biological significance and selectivity towards the oxidant. L-Leucine is an essential amino acid classified as non-polar. It forms active sites of enzymes and helps in maintaining their proper conformation by keeping them in proper ionic states. So oxidation of L-Leucine may help in understanding some aspects of enzyme kinetics.

The Kinetics of oxidation of leucine by a number of oxidants have been reported. Aqueous solutions of amino acids have been oxidized by Mn(VII)[3,4], $KMnO_4$-$MnSO_4$[5], Os(VIII)[6], Ce(IV)[7], Ag(III)[8] etc in various acid and alkaline media in the presence of different catalysts.

Ce(IV) metal ion, being a strong oxidant, is widely used in the oxidation of organic substances, as well as of several inorganic substances[9]. The basic advantage over other oxidants is its reduction to a single substance, cerium (III) without any intermediate reactions. The standard potential of the cerium(IV)-cerium(III) couple changes[10] depending on the complex formation properties of the ligand and it is useful to know the distribution of cerium species in a given medium to explain more clearly the reaction mechanism in kinetic investigations.

In recent years, the use of transition metals such as Os, Ru, Ir, Ag etc either alone or as binary mixtures, as catalysts in various redox processes has attracted considerable interest[11]. The role of Ag(I) as a catalyst is discussed in the studies of M.Adinarayana and B.Sethuram[12]. Metal ions act as catalysts by one of these different paths[13] such as formation of complexes with reactants or oxidation of the substrate itself or through the formation of free radicals. In order to understand the active species of oxidant and catalyst, and to propose the appropriate mechanism, the title reaction is investigated in detail.

EXPERIMENTAL

The kinetic studies of oxidation of Leucine by Ce(IV) in perchloric acid medium has been studied by monitoring Ce(IV). The ceric perchlorate solution was prepared by dissolving ceric ammonium nitrate (B.D.H AnalaR) in perchloric acid (E.Merck) and the solution was standardized by titrating aliquot of the test solution against standard ferrous ammonium sulphate (E.Merck) solution employing ferroin as an indicator. Since the solubility of Leucine in water is low, the solution was therefore prepared in the presence of 0.1 mol dm^{-3} perchloric acid for the higher amino acid concentration. All other reagents were of AnalaR or G.R Merck quality. Doubly distilled water was employed throughout the study. The titration was always done in the presence of 1M H_2SO_4 to obtain clear and stable colour change at the end point.

The reactions were carried out in stoppered Erlenmeyer flasks immersed in a water bath thermostated at 50 ± 0.1^0C. All the components of the reaction mixture except Ce(IV) were taken in the flasks and then allowed to obtain the bath temperature. The reaction was initiated by adding the known volume of temperature pre-equilibrated ceric perchlorate solution. The kinetics were monitored by estimating Ce(IV) in an aliquot (5 cm^3) withdrawn at different intervals of time by titrating against ferrous ammonium sulphate solution employing ferroin indicator[14].

Initial rates were measured employing plane mirror method[15]. Pseudo first order plots were constructed wherever reaction conditions permitted. Triplicate rate measurements were reproducible to within ± 1%.

Stoichiometry

The stoichiometry was determined under experimental conditions of the reaction kinetics.

The reaction with an excess of leucine over Ce(IV) in 1.0 mol dm^{-3} perchloric acid at a fixed concentration of silver(I) was allowed to occur in a thermostated water bath for 24 hours. The product was extracted with diethyl ether from the aqueous solution. The I. R.

Spectrum of the extract indicated the product to be aldehyde, but 2,4,dinitrophenyl hydrazine derivative of aldehyde was not obtained. Since decarboxylation and deamination of leucine takes place, aldehyde is not detected. It appears that NH_3 formed in deamination of leucine reacts with aldehyde and thus remove as an ammonia adduct. So 2,4,dinitrophenyl hydrazine derivative is not obtained. The stoichiometry of the reaction based on the formation of aldehyde can be represented by equation (1).

$$\text{R-CH(NH}_2\text{)COOH} + 2\text{Ce(IV)} \xrightarrow{H_2O} \text{RCHO} + \text{NH}_2 + \text{CO}_2 + 2\text{CE(III)} + 2\text{H}^+ \qquad (1)$$

$\text{R-(CH}_3)_2\text{CH-CH}_2$

The liberated CO_2 was detected by the lime water test.

RESULTS

Variation of cerium (IV)

The concentration of cerium(IV) was varied from 7.5×10^{-4} to 4.5×10^{-3} mol dm^{-3} at three different concentration of Leucine viz 1.0×10^{-2}, 1.5×10^{-2} and 2.0×10^{-2} mol dm^{-3} respectively at $[H^+] = 1.0$ mol dm^{-3}, Ag(I) $= 1.0\times10^{-3}$ mol dm^{-3} and temperature 50^0C. The first order rate constant decreases with increasing concentration of Ce(IV). (Figure 1)

Variation of lysine

The concentration of Leucine was varied from 1.0×10^{-2} to 6.0×10^{-2} mol dm^{-3} at fixed concentration of $[H^+] = 1.0$ mol dm^{-3} , Ag(I) $= 1.0\times10^{-3}$ mol dm^{-3} and temperature 50^0C at three different concentration of Ce(IV) viz 7.5×10^{-4}, 1.0×10^{-3} and 1.5×10^{-3} mol $dm.^{-3}$ The rate of reaction initially increases and then tends towards a limiting value with further increasing concentration of Leucine.

Variation of hydrogen ion

Hydrogen ion concentration was varied from 0.5 to 2.5 mol dm^{-3} employing perchloric acid at fixed con-

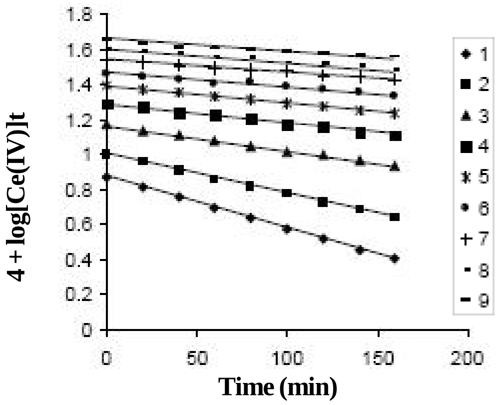


Figure 1 : Pseudo first order plots for The Variation Of Cerium(IV); [Leu]=1.0×10^{-2} mol dm^{-3}, [Ag(I)]=1.0×10^{-3} mol dm^{-3},[H^+] = 1.0 mol dm^{-3}, Temp.= 50^0C, [Ce(IV)] = (1), 0.75×10^{-3} mol dm^{-3}, (2), 1.0×10^{-3} mol dm^{-3}, (3), 1.5×10^{-3} mol dm^{-3}, (4), 2.0×10^{-3} mol dm^{-3}, (5), 2.5×10^{-3} mol dm^{-3}, (6), 3.0×10^{-3} mol dm^{-3}, (7), 3.5×10^{-3} mol dm^{-3}, (8), 4.0×10^{-3} mol dm^{-3}, (9), 4.5×10^{-3} mol dm^{-3}

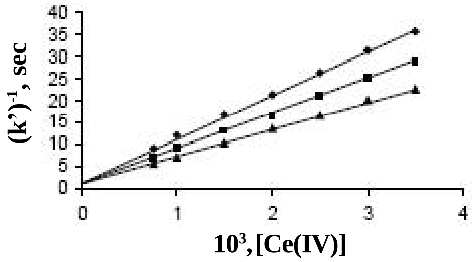


Figure 2: A Plot of (k')$^{-1}$ vs [Ce(IV)]; [H^+] =1.0 mol dm^{-3}, [Ag(I)] = 1.0×10^{-3} mol dm^{-3}, Temp. = 50^0C, [Leu] = (♦), 0.75×10^{-2} mol dm^{-3}, (■), 10×10^{-2} mol dm^{-3}, (▲), 1.5×10^{-2} mol dm^{-3}

centration of Ce(IV) = 1.0×10^{-3} mol dm^{-3},[Leu] =1.0×10^{-2} mol dm^{-3}, Ag(I) = 1.0×10^{-3} mol dm^{-3} and Ionic strength[I] = 2.5 mol dm^{-3} at three different temperatures viz 45^0C, 50^0C and 55^0C respectively. Ionic strength was adjusted by employing $NaClO_4$ First order rate constants initially increases and then tends towards a limiting value with further increasing concentration of hydrogen ion.

Effect of Ionic strength

The effect of Ionic strength on the rate of reaction was studied employing sodium perchlorate at fixed concentration of[Ce(IV)] = 1.0 $\times10^{-3}$ mol dm^{-3}, [Leu] = 1.0×10^{-2} mol dm^{-3}, [Ag(I)] = 1.0×10^{-3} mol dm^{-3} and [H^+] = 1.0 mol dm^{-3} at 50^0C. The rate of reaction increases with increase in ionic strength.

Variation of silver (I)

Silver(I) concentration was varied from 5.0×10^{-4} to 3.0×10^{-3} mol dm^{-3} at constant concentration of[Ce(IV)] = 1.0×10^{-3} mol dm^{-3},[Leu] = 1.0×10^{-2} mol dm^{-3} and[H^+] = 1.0 mol dm^{-3} at 50?C. A plot of pseudo first order rate constant (k') vs[Ag(I)] yields a straight line passing through the origin indicating order with respect to silver(I) to be one.

DISCUSSION

Kinetic investigations of cerium(IV) oxidation in perchloric acid did not indicate complexes[16-19] although Ce^{4+}, $Ce(OH)_2^{2+}$, $Ce(OH)^{3+}$, $(Ce\text{-}O\text{-}Ce)^{6+}$and $(HOCe\text{-}O\text{-}CeOH)^{4+}$ species of cerium(IV) are well established .The polymeric species[20] even of molecular weight more than 40,000 are also reported[21]. The presence of such polymeric species certainly lead to complications in kinetic analysis of the rate data[22]. The species of cerium (IV) depend upon both the concentration of cerium (IV) and perchloric acid. The concentration of polymeric species is significantly less than that of the dimeric species. Baker et al.[23] estimated that 90% of cerium (IV) was present as the monomer in 0.85-2.5 mol dm^{-3} $HClO_{4.}$ McAuley and Z Amzad[18] showed spectrophotometrically that cerium(IV) was present as a monomeric species upto concentration of ~1.5×10^{-3} mol dm^{-3} of cerium (IV) in 1.0 mol dm^{-3} $HClO_{4.}$ So far as the title study is concerned, concentration of cerium (IV) is higher than the concentration limit reported[18] by McAuley et al. Thus the presence of both dimeric and polymeric forms of cerium (IV) with the former being in larger concentration cannot be ruled out. Since the first order rate constant decreases with increasing initial concentration of cerium(IV), such behaviour accounts for the involvement of dimeric and polymeric forms of cerium (IV). The plot of 1 / k' versus[Ce(IV)] (where k' is pseudo first order rate constant) yields a straight line with non zero intercept (Figure 2).

Had polymeric species been in appreciable concentration, the experimental points would have deviated from such a linear relationship. Thus the dimer of cerium (IV) appears to be primary cause of decrease in rate with increasing concentration of cerium (IV) . Such a situation has earlier been observed[24] both in suphuric acid and nitric acid media. The dimerization constant has been reported[21] to be 20.0 at 25^{0}C. Since enthalpy change of dimerization of cerium (IV) is not known, the reported value has been employed in calculation of monomeric cerium (IV) using the relation

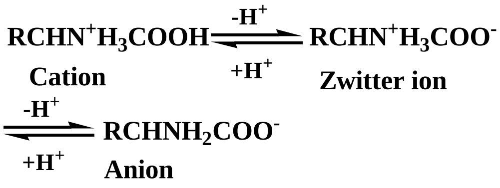
$$[Ce(IV)]_m = [(1+8K_d[Ce(IV)])^{1/2}-1]/4K_d \qquad (2)$$

These estimated monomeric cerium (IV) concentration were further employed in calculation of the first order rate constant. The second order rate constant were then derived from these first order rate constants (TABLE 1).The deviations in second order rate constant can be accounted for the uncertainity in value of Kd employed in the calculation of monomeric forms of cerium (IV)

The amino acids are known to exist in aqueous solutions in the following equilibria (3).

$$RCHNH_2COOH\ (RHNH_2COO^-+H^+)\ RCHN^+H_3COO^- \qquad (3)$$

The dissociation of these acids is pH dependent.



$$\underset{\textbf{Cation}}{RCHN^+H_3COOH} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\textbf{Zwitter ion}}{RCHN^+H_3COO^-} \underset{+H^+}{\overset{-H^+}{\rightleftharpoons}} \underset{\textbf{Anion}}{RCHNH_2COO^-} \qquad (4)$$

Where R=$(CH_3)_2CH-CH_2$

However, the hydrogen ion concentration employed in the reaction is sufficiently high, leucine in view of its pK's should predominantly be in the cationic form.

The rate of reaction increases with increasing silver(I) concentration conforming to a first order dependence with respect to silver(I). However, the order with respect to leucine changes from unity to zero. Such an amino acid dependence can be ascribed to complexation either with Ce (IV) or Ag(I). Amino acids are reported[25] to form an adduct with Ag^I owing to availability of electron pair on oxygen atom[26]. Therefore, it appears that an adduct between Ag^I and leucine is initially formed that on further interaction with Ce(IV) yields another adduct of higher valent silver as is confirmed spectrophotometrically by the addition of 2,2'-bipyridyl in the reaction mixture that yielded a brown orange coloured Ag^{II}-bipy complex with its characteristic absorption maximum at 454 nm[27]. Furthermore, the adduct formation between Ce^{4+} and leucine was ruled out on the premise that the absorbance of Ce^{4+} did not

TABLE 1: Pseudo first order and second order rate constants for the reaction of leucine and cerium(IV) in $HClO_4$ medium.[Ag(I)] = 1.0 × 10^{-3} mol dm^{-3},[H$^+$] = 1.0 mol dm^{-3}, 50^{0}C

10^3[Ce(IV)], mol dm^{-3}	10^2[Leu], mol dm^{-3}	10^5 k?, sec^{-1}	10^5 k, dm^{3}mol^{-1}s^{-1}
0.75	1.0	11.13	8.1
1.0	1.0	8.29	8.0
1.5	1.0	5.98	8.5
2.0	1.0	4.68	8.7
2.5	1.0	3.79	8.7
3.0	1.0	3.18	8.6
3.5	1.0	2.8	8.7
4.0	1.0	2.39	8.4
4.5	1.0	2.18	8.3
0.75	1.5	14.58	10.6
1.0	1.5	10.9	10.4
1.5	1.5	7.59	10.7
2.0	1.5	5.98	10.8
2.5	1.5	4.79	10.8
3.0	1.5	3.99	10.8
3.5	1.5	3.45	10.7
4.0	1.5	3.1	10.8
4.5	1.5	2.8	10.6
0.75	2.0	17.84	13.0
1.0	2.0	14.0	13.4
1.5	2.0	9.59	13.6
2.0	2.0	7.29	13.6
2.5	2.0	5.98	13.6
3.0	2.0	4.98	13.4
3.5	2.0	4.4	13.6
4.0	2.0	3.84	13.4
4.5	2.0	3.6	13.6
10^3[Ce(IV)], mol dm^{-3}	**10^2[Leu], mol dm^{-3}**	**10^5 k?, sec^{-1}**	**10^5 k, dm^{3}mol^{-1}s^{-1}**
0.75	1.0	11.13	8.12
0.75	1.5	14.58	10.6
0.75	2.0	17.84	13.0
0.75	3.0	21.49	15.68
0.75	4.0	23.8	17.37
0.75	5.0	25.33	18.49
0.75	6.0	26.1	19.05
1.0	1.0	8.29	7.95
1.0	1.5	10.9	10.40
1.0	2.0	14.0	13.40
1.0	3.0	16.8	16.12
1.0	4.0	19.2	18.40
1.0	5.0	20.34	19.48
1.0	6.0	21.4	20.54
1.5	1.0	5.90	8.37
1.5	1.5	7.59	10.77
1.5	2.0	9.59	13.62
1.5	3.0	12.28	17.40
1.5	4.0	14.20	20.16
1.5	5.0	15.35	21.79
1.5	6.0	15.73	22.33

change at the addition of excess of leucine.

Considering all these facts along with experimental results and the complex hydrogen ion dependence, a reaction mechanism consisting of steps (4) to (8) can be proposed.

$$Ce^{4+} + H_2O \underset{}{\overset{K_h}{\rightleftharpoons}} CeOH^{3+} + H^+ \quad (5)$$

$$H_3N^+(CH_3)_2CH.CH_2.CH.COOH + Ag^I \overset{K_1}{\rightleftharpoons} [H_3N^+(CH_3)_2CH.CH_2.CH.COOH + Ag^I][Adduct] \quad (6)$$

$$[Adduct] + Ce^{4+} \xrightarrow{k_1} [Adduct]^+ + Ce^{3+} \quad (7)$$

$$[Adduct]^+ \xrightarrow{fast_1} H_3N^+(CH_3)_2CH.CH_2.CHCOO^{\cdot} + Ag^I + H^+ \quad (8)$$

$$H_3N^+(CH_3)_2CH.CH_2.CH.COO^{\cdot} \xrightarrow[fast]{H_2O} NH_3^+(CH_3)_2CH.CH_2.CHO + CO_2 + H^+] \quad (9)$$

The[Adduct]$^+$ undergoes an intramolecular electron transfer yielding product of the oxidation of leucine. The proposed mechanism leads to the rate law (10) or (11)

$$\frac{-d[Ce^{IV}]}{dt} = \frac{k_1K_1[Ce(IV)][Leu^+][H^+][Ag(I)]}{([H^+]+K_h)(1+K_1[Leu^+])} \quad (10)$$

$$\text{or } k' = \frac{k_1K_1[Leu^+][H^+][Ag(I)]}{([H^+]+K_h)(1+K_1[Leu^+])} \quad (11)$$

Where k' and[Leu$^+$] are for pseudo first order rate constant and free equilibrium concentration of leucine respectively. Since the order with respect to silver(I) is one , the rate law (11) further changes to (12).

$$k = \frac{k_1K_1[Leu^+][H^+]}{([H^+]+K_h)(1+K_1[Leu^+])} \quad (12)$$

Where k is an observed second order rate constant.

A plot of 1/k versus[Leu$^+$]$^{-1}$ was made from the equation (12) at constant hydrogen ion concentration that yielded a straight line with non zero intercept (Figure 3). The ratio of intercept and slope of the line yielded the value of K_1 to be 30.3. The value of K_1 obtained in the title reaction in comparison to K_1 = 20 for the Ce^{IV}-glycerol complex[28] in 0.5 mol dm^{-3} $HClO_4$, K_1 = 18 and 29 for Ce^{IV}-cis-1,2-cyclohexanediol and Ce^{IV}-trans-1,2-cyclohexanediol complexes[29] and K_1=22.7 for Ce^{IV}-glysine reaction[30] respectively indicates strong complexation in $HClO_4$ medium.

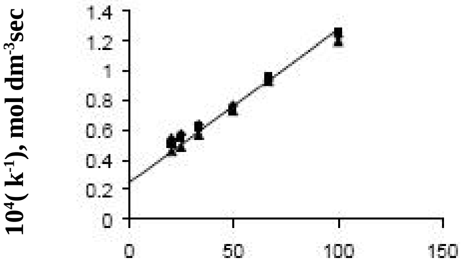


Figure 3 : A Plot of $(k)^{-1}$ vs $[Leu^+]^{-1}$ $[H^+]$ = 1.0 mol dm^{-3}, [Ag(I)] = 1.0 ×10^{-3} mol dm^{-3}, Temp. = 50^{0}C, [Ce(IV)] = (♦), 0.75 ×10^{-3} mol dm^{-3}, (■), 1.0×10^{-3} mol dm^{-3}, (▲), 1.5 × 10^{-3} mol dm^{-3}

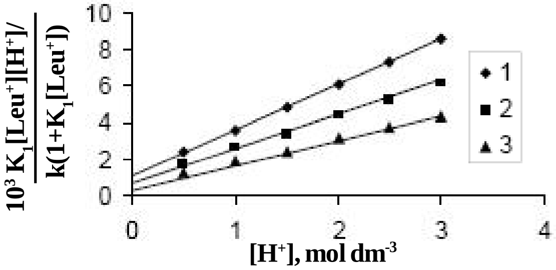


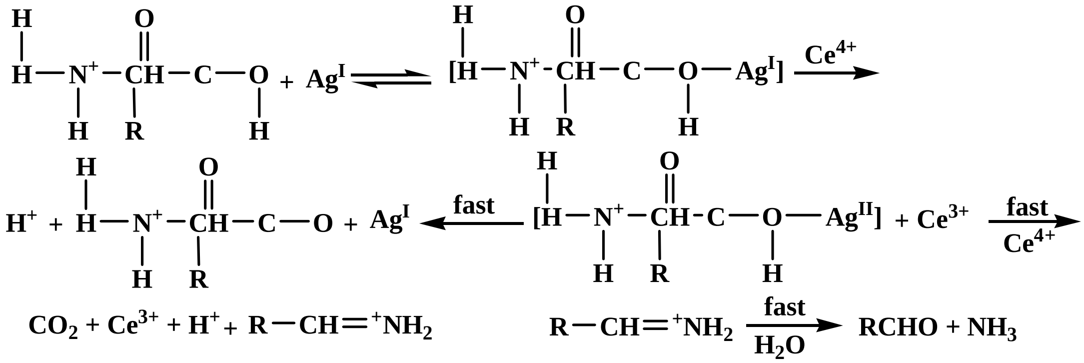
Figure 4 : A plot of $(K_1[Leu^+][H^+]/k(1+K_1[Leu^+]))vs[H^+]$, Temp. = (♦) 45^{0}C , (■) 50^{0}C , (▲) 55^{0}C

Further, rearranging rate equation (12) to (13) when the leucine concentration was kept constant.

$$\frac{K_1[Leu^+][H^+]}{k(1+K_1[Leu^+])} = \frac{[H^+]}{K_1} + \frac{K_h}{k_1} \quad (13)$$

The left hand side function of equation (13) was plotted against[H$^+$] that yielded a straight line with non zero intercept at three temperature (Figure 4). The value of K_h was calculated from the ratio of intercept and slope which came out to be 0.462, 0.488 and 0.528 at 45^{0}C, 50^{0}C and 50^{0}C respectively at[I] = 2.5 mol dm^{-3} .However, there are available in the literature several values of hydrolysis constant of cerium(IV) in $HClO_4$. Amzad and McAuley[18] calculated K_h to be 0.2 ± 0.02 mol dm^{-3} at 25^{0}C that compared well with K_h values of 0.18 (25^{0}C) and 0.11 (5^{0}C) obtained by Offner and Skoog[19]. Moreover, these values of K_h are much closer to the value determined for other M^{4+} aqua ions[31].

If these values are taken into account, the value of K_h obtained kinetically in the title reaction is an agreement when the enthalpy changes for cerium(IV) hydrolytic step are taken into account. k_1 was calculated to be 4.03×10^{-4}, 5.68 ×10^{-4} and 8.13×10^{-4} at 45^{0}C, 50^{0}C



SCHEME

and 55^{0}C respectively.

There is a distinct possibility of electron transfer from leucine to cerium(IV) in presence of silver(I) which can be envisaged from SCHEME 1.

Since the adduct has been considered in scheme, there is no evidence to support the formation of free radicals

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