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KINETICS OF PENTAAMMINECOBALT(III) COMPLEXES OF α -AMINO ACIDS BY CARO'S ACID IN MICELLAR MEDIUM

P. Rajkumar[1,✉], N. Buvaneswari[2], M. Suresh[3], N. Nadeem Afroze[4], B. Andrews[5] and S. Elumalai[6]

[1]Department of Chemistry, Er. Perumal Manimekalai College of Engineering, Hosur-635117,Tamil Nadu, India
[2]Department of Chemistry, Government College of Engineering, Salem- 636011, Tamil Nadu, India
[3]Department of Physics, Er. Perumal Manimekalai College of Engineering, Hosur- 635117,Tamil Nadu, India
[4]PG & Research Department of Chemistry, Islamiah College, Vaniyambadi- 635752, Tamil Nadu, India
[5]Department of Chemistry, P.S.V College of Engineering & Technology, Krishnagiri- 635108,Tamil Nadu, India
[6]Department of Chemistry, Government College of Engineering, Bargur- 635104, Tamil Nadu, India.
✉Corresponding Author: drprajkumar2014@gmail.com

ABSTRACT

The final products of the process are carbonyl compounds, which are produced by the oxidation of pentaamminecobalt(III) complexes of bound and unbound α-amino acids by Caro's acid in a micellar medium. At 32°C, it has been examined. On [α-amino acids] and [Caro's acid], the rate of the reaction exhibits first-order kinetics in both cases. The reaction rate is accelerated by the addition of micelles. After the reaction, a UV-visible spectrophotometer monitors the decline in Co(III)'s absorbance at 504 nm. The reaction's stoichiometry is 0.5 moles of Co(III) α-amino acid complexes using 1.0 mole of Caro's acid, as opposed to 1.0 moles of unbound α-amino acids consuming 1.0 mole of Caro's acid. Acrylonitrile cannot be made to polymerize by reaction. FTIR Spectra have been used to support every one of the freshly synthesized compounds' structural details.

Keywords: α-Amino Acids, Kinetics, Micelles, Oxidation, Stoichiometry, Caro's Acid.

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INTRODUCTION

Comparatively less is known about the kinetic experiments using Caro's acid, a hydrolytic byproduct of Caro's acid in micellar medium, than there is about the oxidation research using its parent analogue.[1-5] There are some processes where it is discovered that Caro's acid's hydrolytic and oxidation reaction rates are equivalent. The kinetics and mechanism of various organic compounds have been studied using a few reviews on halochromates, pyridinium chlorochromate, isoquinolinium fluorochromate, pyridinium fluorochromate, quinolinium fluorochromate, isoquinolinium dichromate, tetrahydropyranyl ethers, and ethylene acetals.[6] A review of the literature reveals that there is no information on the kinetics of Caro's acid's oxidation of α-amino acids in a micelles media. A suitable mechanistic scheme may be envisioned in the current investigation on Caro's acid-induced electron transfer in pentaamminecobalt(III) complexes of -amino acids from the reduction at the cobalt(III) center and yield of carbon-carbon cleavage products. Unbound ligands have also undergone Caro's acid oxidation to support the process, under the same circumstances. Micelles[7] made of Sodium Lauryl Sulfate (NaLS), Cetyltrimethylammonium Bromide (CTAB), and Polysorbate 80 were used in the current study. The bound ligands, such as α-amino acids, dicarboxylic acids, and α-hydroxy acids, have a saturated fragment separating cobalt(III) from the site of initial reaction irradiation of these cobalt(III) complexes. This initial reaction may include a decrease at the cobalt(III) center and, most likely, synchronous carbon-carbon splitting. Kinetic studies on the rates of

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cobalt(III) disappearance in conjunction with rates of cobalt(II) synthesis and organic product production will be useful for carrying out such a process.[8] It is also possible to attempt a qualitative link between quantum yield and the electrical impact.[9,10] The inner-sphere mechanism has progressed the reaction. Comprehensive kinetic and stoichiometric analyses are carried out.[11]

EXPERIMENTAL

Materials and Methods

As ligands, Caro's acid (British Drug House, AnalaR grade) and α-amino acids (Aldrich products were utilized in the form they were obtained) were used. Following Vogel's method, alanine, isoleucine, N-acetyl glycine, and N-benzoyl glycine were produced. The Fan method created the pentaamminecobalt(III) complexes of alanine, isoleucine, N-acetyl glycine, and N-benzoyl glycine as their perchlorates. By using standard techniques, solvents such as ethanol, methanol, ether, and perchloric acid were purified.[12] When the reaction combination of Caro's acid and cobalt(III) complexes of α-amino acids was subjected to product analysis, the yield of cobalt(II) was found to be close to 100%. Using a process described in the literature, the micelles were purified. The commercial samples of the micelles were repeatedly recrystallized from alcohol with the addition of anhydrous ether after being repeatedly washed with anhydrous ether. E. Merck and BDH annular were the only chemicals used, and conductivity water was used to make all of the solutions.[13] By letting reactions take place in glass stopper corning glass jars, the kinetics experiments were conducted. Using starch as an indicator, a solution (5 mL) from the reaction mixture was titrated against sodium thiosulphate. The slope of the tangent obtained at a constant concentration of Caro's acid was used to calculate the reaction rate (-dc/dt) in each kinetic run. The rate measurements for α-amino acids were performed on at2± 0.2°C in a 100% aqueous medium. The synthesis of Caro's acid was also done at four different temperatures. A thermostat that was powered by electricity managed the temperature. The presence of free radicals in the reaction was evaluated in literature by Small amounts of H_2SO_4 were added to maintain ionic strength. Ionic strength and α-amino acid concentrations ranged from [1.0 - 5.0] x 10^2 mol dm^{-3}. Regarding α-amino acids, the reaction is first order. Additionally, second-order plots with similar amounts of micelles and α-amino acids were created. The stated statistics are averages of at least two runs.[15]

RESULTS AND DISCUSSION

(Table-1) explains the kinetic information for the oxidation of α-amino acids by Caro's acid at 0.50 M H_2SO_4 at 32± 0.2°C. Despite the reaction's first-order dependency on Caro's acid, kinetic saturation with respect to substrate concentration has been noted, which points to the possibility of a complex forming between Caro's acid and α-amino acids. In a medium containing micelles, the concentration of cobalt(III) complexes of bound and unbound α-amino acids ranged from [1.0 to 5.0] X 10^2 mol dm^{-3} at a given concentration. The rate constants were repeatable within a 2% range when all kinetic runs were repeated.

Table-1: Kinetic Data for Caro's Acid Oxidation of α-Amino Acids in Micelles

10^2[α-amino acids] mol dm^{-3}	NaLS	CTAB	Polysorbate 80
	$10^4 k_1(s^{-1})$	$10^4 k_1(s^{-1})$	$10^4 k_1(s^{-1})$
Alanine			
1.0	1.135	1.370	1.250
2.0	2.270	2.740	2.500
5.0	5.675	6.850	6.250
Isoleucine			
1.0	1.223	1.426	1.313
2.0	2.446	2.852	2.626
5.0	6.115	7.130	6.565
N-acetylglycine			
1.0	1.587	1.712	1.640
2.0	3.174	3.424	3.281
5.0	7.935	8.560	8.200
N-benzoylglycine			
1.0	1.813	2.234	2.038

2.0	3.626	4.468	4.076
5.0	9.065	11.170	10.190

Caro's acid =1.50 mol dm^{-3}; $[H_2SO_4]$ = 0.50 mol dm^{-3}; [α-amino acids] = [1.0 – 5.0] x 10^2 mol dm^{-3}; [Micelles] = 2.00 x 10^{-3} mol dm^{-3} ; Temperature = 305 K.

The following rate law has been calculated for this reaction using the assumption that Caro's acid and α-amino acid form a 1:1 complex:

$$-d[\alpha\text{-amino acids}] / dt = k_1[\alpha\text{- amino acids}] \quad (1)$$

Table-2 gives the limiting specific rates and formation constants for Caro's acid and α-amino acid complexes. When the carbonyl end is bound by cobalt(III), this complex formation appears to be missing, and the reactions involving Caro's acid and cobalt(III) complexes of α-amino acids exhibit simple second-order kinetics.

Table-2: Kinetic Data for Caro's Acid Oxidation of Pentaamminecobalt(III) Complexes of α-Amino Acids in Micelles

$10^2[(NH_3)_5Co(III)$ - L] mol dm^{-3}	NaLS $10^4 k_1$ (s^{-1})	CTAB $10^4 k_1$ (s^{-1})	Polysorbate 80 $10^4 k_1$ (s^{-1})
Alaninato			
1.0	1.198	1.502	1.397
2.0	2.396	3.004	2.794
5.0	5.990	7.510	6.985
Isoleucinato			
1.0	1.305	1.676	1.402
2.0	2.610	3.352	2.804
5.0	6.525	8.380	7.010
N-acetylglycinato			
1.0	1.708	1.963	1.770
2.0	3.416	3.926	3.540
5.0	8.540	9.815	8.850
N-benzoylglycinato			
1.0	1.975	2.634	2.201
2.0	3.950	5.268	4.402
5.0	9.875	13.170	11.005

Caro's acid = 1.50 mol dm^{-3}; $[H_2SO_4]$ = 0.50 mol dm^{-3}; [Micelles] = 2.00 x 10^{-3} mol dm^{-3}; $[(NH_3)_5$ Co(III)-L$]^2$ = [1.0 – 5.0] x 10^2 mol dm^{-3}; Temperature = 305 K.

One can infer that the oxidation rates of α-amino acids are not greatly impacted by complex formation by comparing the specific rates for Caro's acid oxidation of the different cobalt(III) complexes. This might be the case because the seat of the attack is farther from the cobalt(III) core, where its electrostatic influence on the place of attack is less noticeable. The specific rate of Caro's acid oxidation of Co(III) α-amino acid complexes does, however, change significantly because the two Co(III) centers can have a stronger electrostatic pull on the reactive center. This shows that during the slow step of the reaction, Caro's acid attacks the $-NH_2$ or -NH center, resulting in the production of a radical -NH or -N-. The decrease in the specific rate of Caro's acid oxidation of the cobalt(III) complexes of the α-amino acids alanine, isoleucine, N-acetyl glycine, and N-benzoyl glycine when compared to the unbound ligands suggests that the acyl group has a significant electronic influence and that the Co(III) center's electrostatic influence, specifically on the -NH group, is also present. Since the amino nitrogen is protonated in both the complex and the unbound ligand, the electrostatic influence caused by the ligation of α-amino acids to the Co(III) center appears to be eliminated. However, this electrostatic force may still be present at the set.

Pentaamminecobalt(III) complexes of α-amino acids and unbound ligands underwent stoichiometric study[16] for Caro's acid oxidation in the presence of micelles at 32± 0.2°C (Table-3). Iodometry and spectrophotometry were used to determine Caro's acid concentration from the change in absorbance

measured at 502 nm. After applying the necessary blank corrections for the breakdown of Caro's acid and aquation of Co(III) complex of α-amino acids in the presence of micelles, [Caro's acid] was calculated. For the unbound ligand, a comparable calculation about [Caro's acid] was also produced.

Table-3: Stoichiometric Data for Caro's Acid Oxidation of Cobalt(III) Bound & Boundless A-Amino Acids in Micelles

10^3[Compound] mol dm^{-3}	10^2[Caro's acid]$_{initial}$ mol dm^{-3}	10^2[Caro's acid]$_{final}$ mol dm^{-3}	$\Delta 10^3$[Caro's acid] mol dm^{-3}	[Compound]: Δ[Caro's acid]
Alanine				
1.0	1.0	0.99	1.01	1.00: 1.00
2.0	2.0	1.90	1.90	1.00: 0.90
Isoleucine				
1.0	1.0	0.90	1.10	1.00: 1.10
2.0	2.0	1.95	2.02	1.00: 1.05
N-acetylglycine				
1.0	1.0	0.98	1.00	1.00: 0.99
2.0	2.0	1.95	1.99	1.00: 0.97
N-benzoylglycine				
1.0	1.0	0.98	1.05	1.00: 1.08
2.0	2.0	1.90	2.00	1.00: 0.95
Alaninato				
1.0	1.0	0.95	0.50	2.00: 0.97
2.0	2.0	1.95	1.05	2.00: 1.00
Isoleucinato				
1.0	1.0	0.99	0.51	2.00: 1.10
2.0	2.0	1.99	1.02	2.00: 1.02
N-acetylglycinato				
1.0	1.0	0.95	0.50	2.00: 0.97
2.0	2.0	1.90	1.00	2.00: 1.00
N-benzoylglycinato				
1.0	1.0	0.95	0.50	2.00: 1.00
2.0	2.0	1.99	1.10	2.00: 1.05

Caro's acid = 1.50 mol dm^{-3}; $[H_2SO_4]$ = 0.50 mol dm^{-3}; [Micelles] = 2.00 x 10^{-3} mol dm^{-3}; $[(NH_3)_5 Co (III)\text{-}L]^2$ = [1.0 – 5.0] x 10^2 mol dm^{-3} ; Temperature = 305 K.

The ratio of the reacted [oxidant] and [substrate] was used to compute the stoichiometry. The amount of cobalt(III), carbonyl compound, and cobalt(III) keto acid complex were then compared to this value. The outcomes proposed that for 1.0 mole of cobalt(III) complex, about 0.5 mole of Caro's acid is consumed, whereas with the unbound ligands for 1.0 mole of α-amino acids about 1.0 mole of Caro's acid is consumed.

Effect of Ionic Strength

Using a suitable combination of α-amino acids and sulphuric acid, the kinetic investigation was studied at different ionic strengths of 1.0, 2.0, and 5.0. In (Table-4), the rate constants are listed.

Effect of Temperature

While maintaining other experimental conditions constant, the kinetics of the oxidation of α-amino acids by Caro's acid was studied at four different temperatures (305 K, 307 K, 309 K, and 311 K). It is discovered that the Arrhenius plot of log k_2 versus 1/T is linear. Using the Arrhenius and Eyring plots, the enthalpy, entropy, and free energy of activation were determined from k_2 at 305, 307, 309, and 311 K. Lactic acid oxidation was determined to have the following thermodynamic parameters: -H# = 66.69 0.5 kJ/mol, -S# = 145.79 3.5 J/K/mol, and -G# = 88.76 1.5 kJ/mol.

Polymerization of Acrylonitrile

Acrylonitrile did not polymerize when α-amino acids were oxidized by Caro's acid in a nitrogen environment. In addition, the rate was unaffected by the addition of acrylonitrile. The reaction

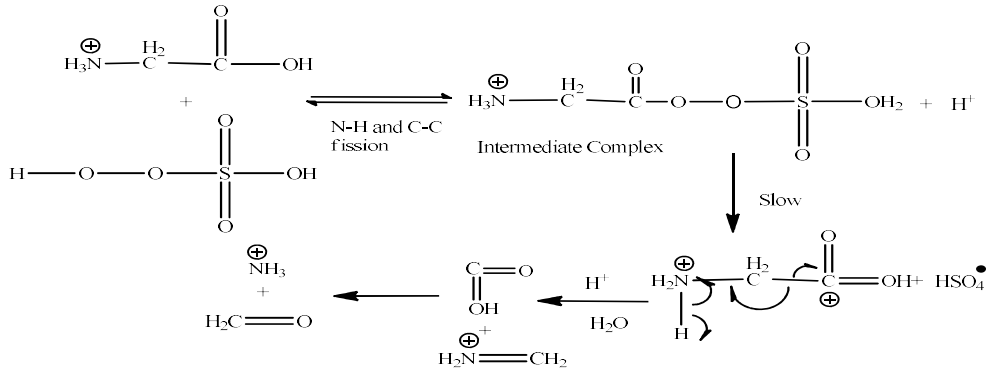
mechanism[17] could confirm the absorption of free radicals. According to (Scheme-1), when 100% of HCHO is produced, Caro's acid oxidizes the -NH center and causes the creation of a radical that, in a subsequent phase, undergoes carbon-carbon bond fission to produce Co(II).[18] The creation of a nitrogen radical is suggested in (Scheme-2), which would then react with Caro's acid in succeeding steps to produce the Co(III) complex of α-amino acids.

Table-4: Kinetic Rate Data for Oxidation of α-Amino Acids in Sulphuric Acid at Constant Ionic Strength

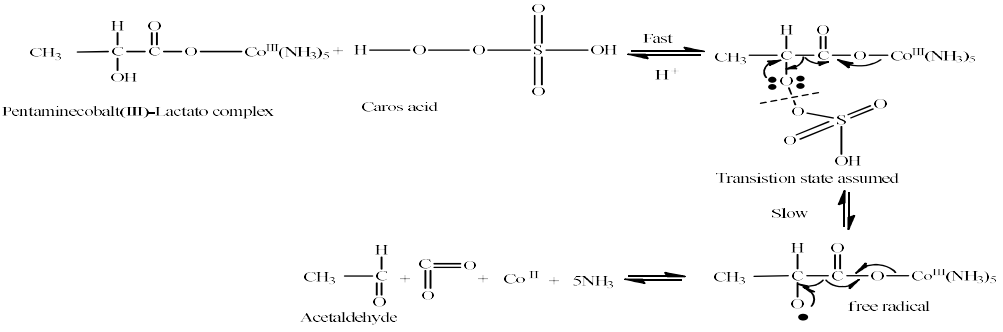
10^3 Substrate	$[H_2SO_4]$	10^3k_1 s^{-1}
Alanine	1.0	2.952
	2.0	2.989
	5.0	2.972
Isoleucine	1.0	3.812
	2.0	3.803
	5.0	3.869
N-acetyl glycine	1.0	3.512
	2.0	3.560
N-benzoyl glycine	5.0	3.573
	1.0	4.012
	2.0	4.087
	5.0	4.056

Caro's acid =1.50 mol dm^{-3}; $[H_2SO_4]$ = 0.50 mol dm^{-3}; [α-amino acids] = [1.0 – 5.0] x 10^2 mol dm^- ; Temperature = 32 ±0.2°.

According to the reported stoichiometric values, in this instance, 1.00 moles of Co(III) should consume 1.00 moles of Caro's acid. The amount of Caro's acid consumed when dealing with unattached α-amino acids is roughly 0.5 mole.



Scheme-1



Scheme-2

Spectral Details

The IR spectral data for the pentaamminecobalt (III) nitrate complex (Fig.-1) reveals that five NH3 groups have wavelengths of 3730, 3797, 3834, 3878, and 3936 cm^{-1}. The presence of the aforementioned compound is indicated by the following parameters: 3286 cm^{-1} for the OH group, 2538 cm-1 for the -C-H group, 1627 cm^{-1} for the C=C group, and 1377, 1317 cm^{-1} for the in and out plane bending of the N-H

group. The IR spectral data for acetaldehyde (Fig.-2) demonstrates that the existence of the compound can be detected in the bands at 2720 and 2810 cm^{-1} for the -CH_3 group, 1730 cm^{-1} for the C==O group, and 1360 cm^{-1} for the -C-H group. The different reactant complexes conduct an electron transfer process both in the presence of catalysis, such as Caro's acid, and in the absence of micelles, as shown by both spectrum features.

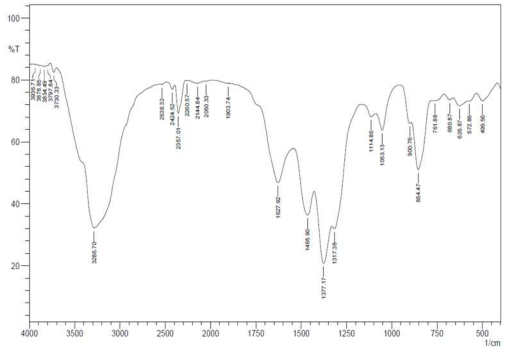


Fig.-1: FTIR Spectrum of Carbonatopentaamminecobalt (III) Nitrate

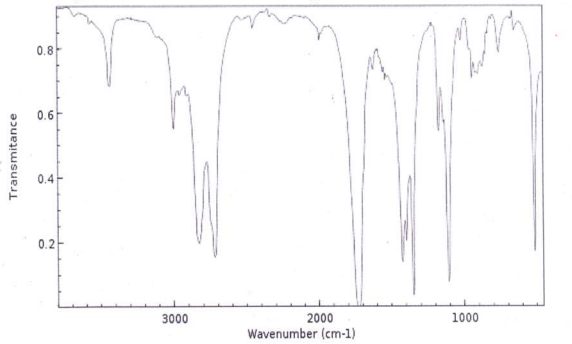


Fig.-2: The IR Spectral Data for Acetaldehyde

As shown by the spectral analysis, the existence of reactant complexes prior to titration or reaction is evident in Fig.-1 and Fig.-2. These spectral details clearly show that the inner sphere or electron transfer has occurred because the product spectrum data in Fig.-2 indicates the existence of acetaldehyde. As a result, an accurate product of acetaldehyde was created.

CONCLUSION

In the presence of NaLS, CTAB, and Polysorbate 80 in a micelles media, an induced electron transfer reaction has been attempted with Caro's acid of pentaamminecobalt (III) complexes of both bound and unbound α-amino acids. Second-order kinetics can be seen in the reaction. In these reactions, the rate of oxidation in [α-amino acids], $[(NH_3)_5$ Co(III)-L$]^2$, and [Caro's acid] each exhibit first-order kinetics. For the oxidation of complexes and free ligands in three different (Anionic, Cationic & Neutral) micelles mediums, product and stoichiometric analysis is conducted. As the concentration of the micelles increases, a rise in the rate is seen. It explains the synchronized decarboxylation, electron transfer, and C-C bond fission to the cobalt(III) center. The additional micelles speed up a reaction's rate of oxidation. The CTAB micelle reacts more quickly than the NaLS and Polysorbate 80 micelles among the three. The Caro's acid results are extremely appealing and demonstrate the new reagent's value as a supplement to the already-existing oxidizing agents. A hypothesized process involved the complex transferring one electron and the ligand transferring two electrons. While 1.0 mole of unbound α-amino acids consumes 1.0 mole of Caro's acid, 1.0 mole of cobalt(III) complexes of α-amino acids consume 0.5 mole of Caro's acid. No polymer is produced, demonstrating that no radicals were created throughout the reactions. Arrhenius plots showing the linear relationship between log k_2 and 1/T arise from the oxidation of α-

amino acids by Caro's acid. The appropriate methodology has been used. FTIR Spectra were used to confirm the products.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing / editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

P. Rajkumar https://orcid.org/0000-0001-5291-4347
N. Buvaneswari https://orcid.org/0000-0002-4297-0289
M. Suresh https://orcid.org/0000-0001-6881-9029
N. Nadeem Afroze https://orcid.org/0000-0003-4049-1812
B. Andrews https://orcid.org/0009-0002-0546-7868
S. Elumalai https://orcid.org/0009-0005-8688-2132

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