Kinetics and Mechanism Studies of Reaction of Some Amides with Cerium (IV) in Acid Medium

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Abstract

The kinetics and mechanism of reaction of some amides (Acetamide, N-phenylacetamide, N-phenylbenzamide) with Cerium (IV) have been studied in acid medium of sulphuric acid. The uv-vis, spectrophotometric technique was used to follow up the reaction in the selected wavelength to be followed was 320nm. The kinetic study showed that the reaction is first order for Ce(IV) and zero order for amides. The effect of using different concentrations of sulphuric acid on the rate of reaction had been studied and no effect was observed. A precipitate had been formed as a product of reaction. Organic tests and spectroscopic identification have been done, which showed that the final product was a complex. This complex formed as a result of linkage between Ce(IV) and the carbonyl group of amide.

Introduction

Cerium element is one of the most spread lanthanides elements. It has numerous oxidation states (+4, +3, −2)[1]. Ce(IV) ion is considered as one of important oxidants. Since its reduction potential was found in sulphuric acid solution of (1-8)N equal 1.44volt, this potential value is different according to the difference of acidic media which contains[2]. Ce(IV) solution in acidic media is stable for long time and is not influenced by light and increasing temperatures for short time[3]. Ce(IV) ion in sulphuric acid solution gives an absorption peak in ultra violate area at 320nm in which Ce(IV) ion consumption can be followed up. There are many reports in literature about reaction of Ce(IV) with organic compounds[4-7],but there was no results reported for reaction between Ce(IV) and amides.

Experimental

Materials: Cerium(IV) sulphate supplied by Riedel-de Hean of 96% purity , Acetamide supplied by Aldrich of 98 % purity,N-phenyl acetamide supplied by Fluka of 95% purity , N-phenyl benzamide supplied by Seema of 98% purity, Sulphuric acid supplied by BDH of 98% purity and double distillated water had been used.

Method: The reaction was followed up throughout consuming the concentration of Ce(IV) ion in the ultra violate absorption area at wavelength of 320nm. The reaction was carried out by adding 2.5ml of Ce(IV) solution of different concentrations in quartz cell (1×1)cm and adding 60µl of different concentrations of amides solutions. The absorption was recorded directly after mixing the materials quickly. Then, the absorption was determined in successive intervals. The reaction was carried out in different concentrations of sulphuric acid.

Results and Discussion

Kinetics measurement: The kinetics of reaction of amides with Ce(IV) ion was studied at 25°C. The study showed that the reaction was first order by using the absorption as function for the concentration of Ce(IV) in first order equation

$$\ln (A_t - A_\infty) = \ln (A_0 - A_\infty) - kt$$

Where A_∞, A_0, A_t are absorption at the end of reaction, before reaction started and at particular time respectively.

The results showed that the values of rate constant for first order remained constant at changing the concentrations of Ce(IV). The other parameters were kept constant , as it is shown in table (1) and figures (1-3). This indicates that the reaction is first order with respect to Ce(IV).

The rate constant was the same value with changing the concentration of amides, as shown in Table (1). This indicates that the reaction is zero order with respect to amides. No effect was observed on rate constant value when the concentration of hydrogen ion was changed.

Stoichmetery: Stoichmetery measurements, by iodometric titration, showed that each mole of Ce (IV) reacts with 2 mole of amides.

Identification of product: The reaction was carried out at high concentrations of reactants. The mixture was left for 24 hours to ensure completion the reaction and a precipitate was observed as a product of the reaction. The precipitate was dissolved by ethanol, and some organic tests were done on the precipitate like the test used for aldehydes by using dinitrophenylhydrazine as indicator, and the test used for carboxylic acid

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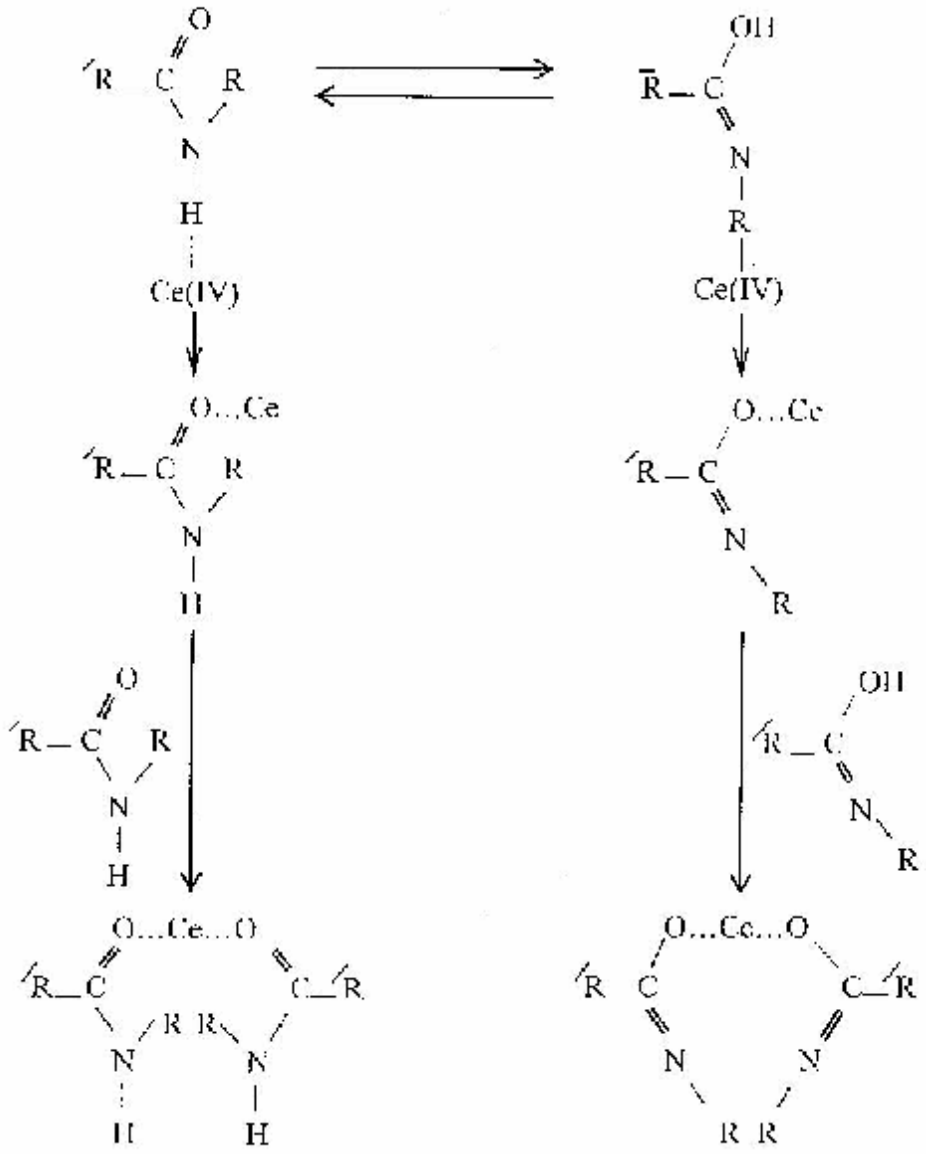
using sodium carbonate, the results for both tests were negative. the I.R spectrum of product of the reaction between Ce(IV) and N-phenylbenzamide was recorded, figure(4). The I.R spectrum showed the presence of all band of N-phenylbenzamide along with the presence of C O-M band (500-510)cm^{-1} which indicated the link

of Ce(IV) with amides which took the form of a complex.

Suggested Mechanism: Depending on kinetic results, identification of the product and some mechanisms in the literature[6], the following mechanism was suggested:



Suggested rate expression: Literature[8] showed that Ce(IV) makes a complex when dissolved in sulphuric acid as follows:

$$Ce(SO_4)_2 + 2HSO_4^- \rightleftharpoons H_2Ce(SO_4)_4^{2-} \quad \ldots\ldots(1)$$

This study showed the concentration of sulphuric acid had no effect on the rate of reaction. Depending on kinetic result $H_2Ce(SO_4)_4$ the dis lin

$$H_2Ce(SO_4)_4^{2-} + \text{Amide} \xrightarrow[\text{slow}]{k_1} \text{complex} \quad \ldots\ldots(2)$$

$$\text{complex} + \text{Amide} \xrightarrow{k_2} \text{product} \quad \ldots\ldots(3)$$

The rate law depending on k_1 step

$$R = k_1\left[H_2Ce(SO_4)_4^{2-}\right][\text{Amide}] \quad \ldots\ldots(4)$$

the experimental data showed that the order of amide was zero order, the final rate equation of the reaction:

$$R = -\frac{d[Ce]}{dt} = k_1\left[H_2Ce(SO_4)_4^{2-}\right] \quad \ldots\ldots(5)$$

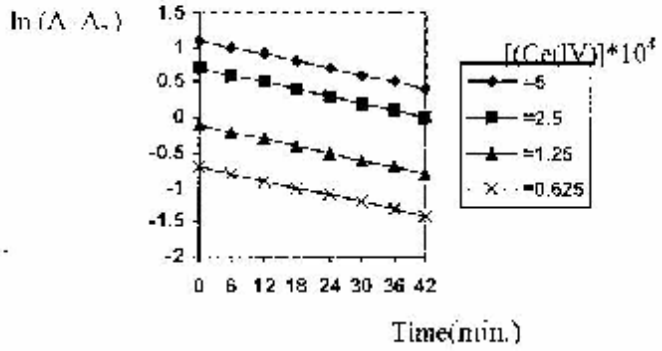


Fig. (1): A plot of ln (A_t-A_∞) against time for reaction between Ce(IV) of different concentration and 1M acetamide

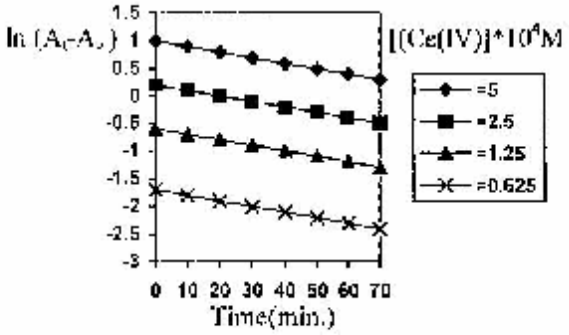


Fig. (2): A plot of ln (A_t-A_∞) against time for the reaction between Ce(IV) of different concentration and 0.001 M N-Phenylbenzamide

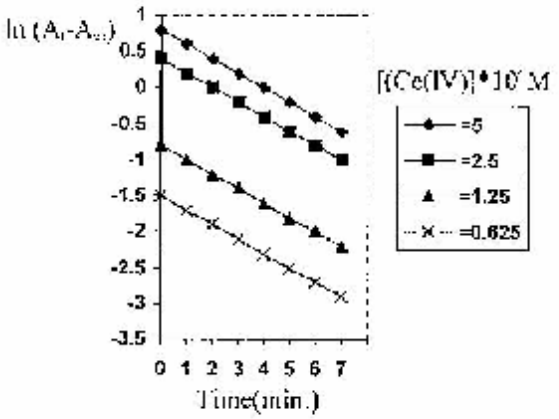
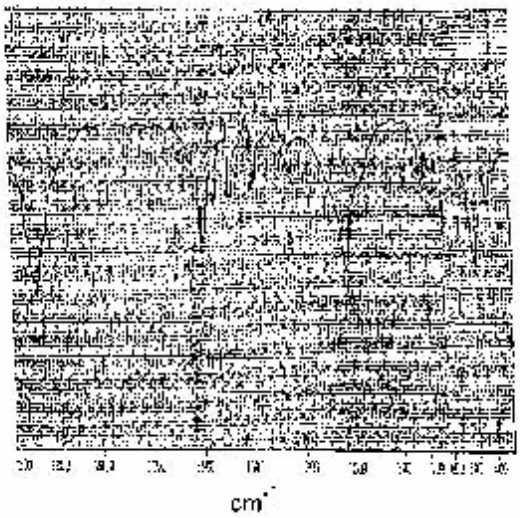


Fig. (3): A plot ln (A_t-A_∞) against time for the reaction between Ce(IV) of different concentration and 0.01M N-Phenylacetamide



Figure(4): I.R spectrum of product of reaction between Ce(IV) and N-phenylbenzamide

Table (1)
The values of rate constant and concentration of reactants

[Ce(IV)] *10⁴/M	[Acetamide]/M	k*10²/min⁻¹
5		1.63
2.5	1	1.51
1.25		1.71
0.625		1.67
	1.5	1.52
2.5	1	1.51
	0.75	1.7
	0.2	1.65
[Ce(IV)] *10⁴/M	[N-phenylbenzamide] *10²/M	k*10² / min⁻¹
5		1.5
2.5	1.1	1.48
1.25		1.5
0.625		1.43
	1.1	1.48
2.5	0.8	1.52
	0.5	1.46
	0.2	1.55
[Ce(IV)] *10⁴/M	[N-phenylacetamide] *10²/M	k*10² / min⁻¹
5		3.2
2.5	1.1	3.36
1.25		3.26
0.625		3.31
	1.9	3.28
2.5	1.4	3.32
	1.1	3.36
	0.7	3.29

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