

KINETICS OF OXIDATION OF SOME NITROGEN AND SULFUR COMPOUNDS

ABSTRACT

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1. KINETICS OF OXIDATION OF SOME ALIPHATIC AMINES
BY ALKALINE HEXACYANOFERRATE (III)

The kinetics of oxidation of some aliphatic amines (methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine and triethylamine) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of these reactions were found to be dependent on the first powers of the concentrations of both, substrate and oxidant. The rate of the reaction was independent of the concentration of alkali in the range studied, for methylamine and dimethylamine. An alkaline pH was necessary for the facile oxidation of these amines. Though there was no dependence on [alkali] over the pH range studied, the reaction was not independent of pH, in the wider sense.

All the other amines (trimethylamine, ethylamine, diethylamine and triethylamine) underwent facile oxidation by aqueous hexacyanoferrate (III) in neutral medium, that is, without using any alkali.

The effect of changes in temperature on the rates of the reactions has been studied, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium,

changes in the concentrations of added hexacyanoferrate (II) ions, and the addition of salts, did not have any effect on the rates of these reactions.

The presence of radical intermediates, formed in the rate determining step of the reaction, has been detected and characterized by ESR spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of radical intermediates in the rate determining step. The radical underwent further reaction to yield the products. The products formed from the oxidation of methylamine, dimethylamine and trimethylamine were the respective N-acyl derivatives. The products from the oxidation of ethylamine, diethylamine and triethylamine, were the respective dealkylated products. These products were characterized by analytical and spectral methods.

2. KINETICS OF OXIDATION OF SOME AROMATIC AMINES BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of some aromatic amines (aniline and substituted anilines, N-methylaniline, N-ethylaniline, N,N-dimethylaniline, N,N-diethylaniline, benzylamine and substituted benzylamines, diphenylamine and substituted diphenylamines) by potassium hexacyanoferrate (III), in alkaline medium, at constant ionic strength, under a nitrogen

atmosphere, has been studied.

The rates of these reactions were dependent on the first powers of the concentrations of both, substrate and oxidant. The rate of the reaction was independent of the concentration of alkali in the range studied. An alkaline pH was necessary for the facile oxidation of these amines.

The reactions were influenced by changes in the temperature, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium, changes in the concentrations of added hexacyanoferrate (II) ions, and the addition of salts, did not have any effect on the rates of these reactions.

Increasing proportions of methanol resulted in an increase in the rate of oxidation, in the case of aniline and diphenylamine. In the case of N,N-dimethylaniline, the reverse trend was observed. Plots of $\log k_{\text{obs}}$ against the reciprocal of the dielectric constant were linear, indicating that the reactions under consideration were of the ion-dipole type.

The introduction of electron-releasing groups caused an increase in the rate of the reaction, whereas electron-withdrawing groups caused a decrease in the rate of the reaction. Hammett plots of $\log k_{\text{obs}}$ against σ^+ (or σ) were linear, with the values of $\rho^+ = -1.0$ (anilines), and $\rho = -1.0$ (for diphenylamines and benzylamines). The ρ values for these substrates (anilines, diphenylamines and

benzylamines) were in the range for processes wherein the rate determining step involved the formation of radical intermediates.

The oxidation of benzylamine - α -d₂ exhibited a kinetic isotope effect, with $k_H/k_D = 6.3$, indicating a cleavage of the C-H bond of the methylene group attached to the aryl ring, resulting in the formation of a radical intermediate in the rate - determining step of the reaction.

The presence of radical intermediates was detected and characterized by ESR spectroscopy.

The reaction pathway has been mechanistically visualized as proceeding via the formation of a radical intermediate in the rate determining step. The radical was rapidly converted to the products. Efforts to isolate intermediate product(s) were not successful.

The products obtained from the oxidation of the various aromatic amines, were:

- (a) azobenzene (80-85%), from the oxidation of aniline;
- (b) formanilide (70%) from the oxidation of N-methylaniline;
- (c) formanilide (70%) and formaldehyde (10%), from the oxidation of N-ethylaniline;
- (d) N-methylformanilide (75%), from the oxidation of N,N-dimethylaniline;
- (e) formanilide (70%), acetaldehyde (10%) and formaldehyde (10%),

from the oxidation of N,N-diethylaniline;

(f) tetraphenylhydrazine (80%), from the oxidation of diphenylamine;

(g) benzaldehyde (80%) and ammonia, from the oxidation of benzylamine.

The products formed, in each case, were isolated and characterized by analytical and spectral methods.

3. KINETICS OF OXIDATION OF SOME INORGANIC SULFUR COMPOUNDS BY ALKALINE HEXACYANOFERRATE (III).

The kinetics of oxidation of some inorganic sulfur compounds (sulfite, metabisulfite, dithionite, thiosulfate and thiocyanate) by potassium hexacyanoferrate(III), in alkaline medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of the reactions were observed to be dependent on the first powers of the concentrations of each, substrate and oxidant. The rates of the reactions were dependent on the first powers of the concentrations of alkali in the range studied, in the case of sulfite, metabisulfite and dithionite ions. In the case of thiosulfate and thiocyanate ions, the rates were independent of the concentrations of alkali in the range studied.

The rates of the reactions were influenced by changes in temperature, and the activation parameters have been evaluated.

Variations in the ionic strength of the medium, and changes in the concentrations of added hexacyanoferrate (II) ions, did not have any effect on the rates of these reactions.

Radical intermediates were detected in the oxidation reactions of sulfite, dithionite and thiocyanate ions.

The mechanistic pathway envisaged the formation of radical intermediates, in the case of the oxidation of sulfite, dithionite and thiocyanate ions. Rapid dimerization yielded the products, which were isolated and characterized. In the oxidation of thiosulfate, the intermediate anion underwent rapid dimerization to yield the product, which was isolated and characterized.

4. KINETICS OF OXIDATION OF SOME ORGANIC SULFUR COMPOUNDS BY ACIDIC HEXACYANOFERRATE (III).

The kinetics of oxidation of some organic sulfur compounds (thiomalic acid, thioglycolic acid and thiophenol) by potassium hexacyanoferrate (III), in acidic medium, at constant ionic strength, under a nitrogen atmosphere, has been studied.

The rates of the reactions showed a first order dependence on the concentrations of each, substrate and oxidant. The rates of the reactions showed a first order dependence on the concentration of acid (in the case of thioglycolic acid and thiophenol), but showed an inverse dependence on the concentration of the acid, in the case of thiomalic acid.

The rates of the reactions were enhanced, with an increase in the temperature of the medium. The activation parameters have been evaluated.

Increasing proportions of methanol resulted in an increase in the rate of the reaction, in the case of thiophenol. A plot of $\log k_{\text{obs}}$ against the reciprocal of the dielectric constant was linear, indicating that the reaction was of the ion-dipole type.

Variations in the ionic strength of the medium, changes in the concentrations of added hexacyanoferrate (II) ions, the addition of salts, and the addition of the product itself, did not have any effect on the rates of these oxidation reactions.

The presence of radical intermediates was detected and characterized by ESR spectroscopy.

The mechanism of the reaction involved the formation

of radical intermediates in the rate determining step. The subsequent step involved a rapid dimerization of the radical, to yield the respective disulfide. The products formed have been characterized by analytical and spectral methods.

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