KINETIC STUDIES ON REACTIONS OF SOME NITROGEN COMPOUNDS

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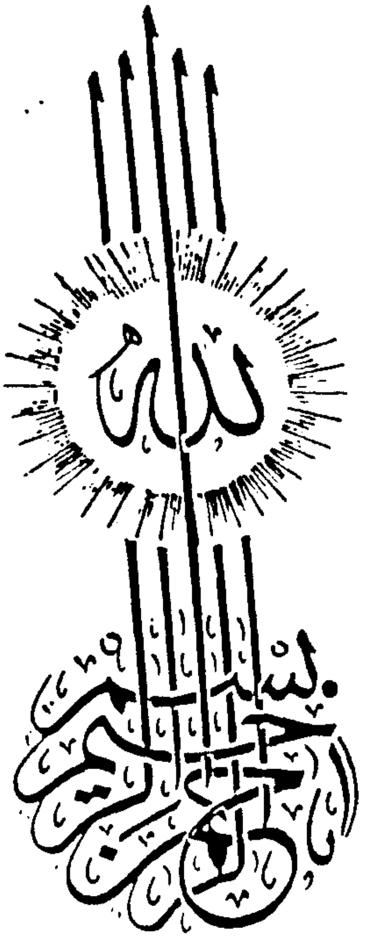

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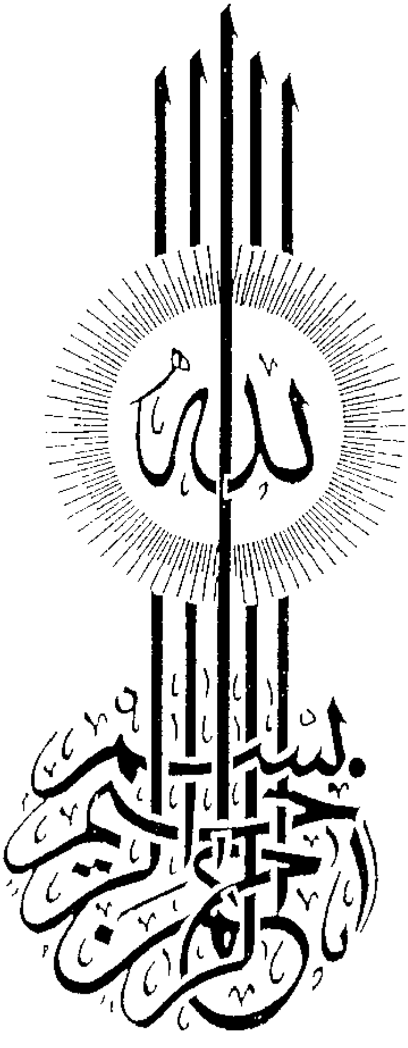
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بسم الله الرحمن الرحيم

KINETIC STUDIES ON REACTIONS OF SOME NITROGEN COMPOUNDS

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NOTE

The candidate has attended courses for one year in physical and inorganic chemistry covering the following topics:-

1. Advanced surface chemistry.
2. Advanced electrochemistry.
3. Statistical thermodynamics.
4. Quantum chemistry.
5. Solvent extraction.
6. Nuclear chemistry.
7. Inorganic reaction mechanism.
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9. Analytical chemisty

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Object Of Investigation

In view of the prime importance of amines in industry as raw materials, intermediates and finished products, and their uses in the laboratory, there is always a continuous interest in the analytical problems relevant to them.

The present investigation is an extended interest in this direction, in which a simple, sensitive and selective spectrophotometric method for aromatic amine assessment is developed in the light of a careful kinetic study of the interaction between certain aromatic amines and p-benzoquinone reagent. A comprehensive systematic study of the various factors affecting the rate of the reaction was investigated, viz. initial concentration of the reactants, temperature, time and polarity of solvent. The rate of reaction was studied using the initial rate method.

CHAPTER 1

INTRODUCTION

HISTORICAL INTRODUCTION

ON

(A) Determination of Aromatic Amines

The wide distribution of amines in nature, their importance in industry as raw materials, intermediates and finished products, and their uses in the laboratory present continuous interest in the analytical problems relevant to them.

Spectrophotometry is commonly used for determination of low levels of various amines. The various methods usually applied for determination of amines may be conveniently classed according to the analytical techniques adopted into:

(i) potentiometric titration methods, (ii) spectrophotometric methods, (iii) volumetric methods, besides other specific determination methods for certain amines. In the following, a historical survey on the various methods used is given.

(1) Potentiometric titration methods:

Glass calomel electrode system is most frequently used for titration of amines in aqueous and non-aqueous media. A silver-silver chloride electrode may be used instead of calomel, electrode. Singh and Ahusanulhaque(1) in (1942) estimated some O-, and p-aromatic amines on the millimole level by potentiometric titration with KIO_3 in presence of HCl or HNO_2.

According to Matrka(2) and saxena et al(3) aromatic amine salt can be determined by nitrous acid under improved conditions using pt-calomel or pt-Ni electrodes for potentiometric titration.

Chloramine B(4) as brominating agent can be used potentiometrically for determination of both aromatic amines and phenols.

Takeuchi et al (5) determined the primary aromatic amines by diazotization reaction potentiometrically using a glassy-carbon electrode as indicator electrode and the reference electrode was "pt" wire. A differential titration curve was used to determine the end point. The end point varied with the quantity of HCl added and with the concentration of KBr added.

Several aliphatic and aromatic amines were titrated potentiometrically with $HClO_4$(6) in some organic solvents such as AcOH, MeCN, MeOH, $PhNO_2$ and iso-BuCoMe. Abetter titration curve was obtained by adding a very small amount of diethylaniline perchlorate to the amine solution. The two electrodes were made of the same metal. The ionization constant of diethylamine as well as the equilibrium constant of the reaction:

$$\bar{ClO_4}Di\ H^+ + B \rightleftharpoons BH^+\ ClO_4^- + Di$$

in which Di is diethylaniline and B is an amine were calculated by assuming that ion pairs were present in AcOH.

According to Jander et al(7) metallic were electrodes such as "Au" and "Ag" can be used as electrodes for determination of the aromatic amines potentiometrically in anhydrous acetic acid using $HClO_4$ as a titrant. $PhNEt_2$, C_5H_5N, $PhNH_2$, $PhNMe_2$ and 1-naphthylamine have been determined by this procedure.

Aromatic primary amines and compounds containing reactive methylene groups can be determined potentiometrically using a "pt" spiral indicator electrode and a saturated calomel reference electrode and $BuNO_2$ or $EtNO_2$ solution as a titrant(8). The decomposition of HNO_2 is avoided, since it is consumed in both reactions (diazotization or nitrozation) at a rate almost equivalent to the rate of hydrolysis of $BuNO_2$ or $EtNO_2$.

The determination of aromatic amines by titrations with $NaNO_2$ in acid medium can be followed potentiometrically$^{(9,10)}$ and electrometrically$^{(11)}$. In the potentiometric method pt /calomel electrodes were used and the average inflection was 0.585 V. HCl concentration must be maintained at 7-10 gm/25 ml and the temperature $< 20^{o}C$. In the electrometric method, the well known "dead stop" end point method was used for this determination. This method has been applied to a wide variety of compounds including mono, di and trisubstituted derivatives of aniline and "α" and "β" naphthylamine.

Litivinenko et al$^{(12)}$ were able to determine the primary aromatic amines by potentiometric titration with $NaNO_2$ in acid media in presence of KBr acting as diazo-catalyst. The equivalent point is at the maximum jump in potential $\Delta E/\Delta V$. The percentage of amine can be calculated from the following equation: % amine = $a.T \frac{100}{b}$ where "a" is the number of ml of $NaNO_2$ used "T" is the titre of the $NaNO_2$ standaridized against an amine and "b" is the weight of the sample. Sulfanilic acid, aniline, p-nitroaniline, m-nitroaniline, 4-aminobiphenyl, 4-amino-4̀-nitro-2,2̀ dichlorobiphenyl and benzidine have been satisfactorily determined by this procedure.

A platinum-tungestem bimetallic electrode system(13) can be used for the estimation of the organic compounds such as primary aromatic amines and phenols dissolved in a suitable solvent e.g. (dil H_2SO_4, H_2O, ACOH, EtOH); a standard bromide mixture ($KBrO_3$ + KBr) used as titrant. Aniline, O-aminobenzoic, phenol, sulphanilic acid and O-cresol were determined by this procedure.

Sensi and Co workers(14) used the potentiometric titration technique for the analysis of aorganic compounds such as alkali earth salts of organic acids e.g. sodium benzoate, primary secondary and tertiary amines e.g. aniline, O- phenylenediamine, aminoacids p-aminosalicylic acid and anthranilic acid. Potential measurements were carried out by means of a glass electrode used with an "ionisis ionometer".

In (1974) Hassan(15) used the chloride electrode as an ion selective electrode for microdetermination of the amino group in aryl amines, e.g.p-aminobenzoic acid, anthranilic acid , and O-phenylenediamine after reaction with HCl (g) in ether either by direct measurement or by potentiometric titration with $AgNO_3$.

Aromatic amines and phenols were determined by potentiometric titration with bromine in propylene carbonate(16) as a medium, using a pt foil indicating electrode versus a reference electrode of Ag -0.1 M $AgClO_4$ in propylene carbonate. A base such as pyridine must be present to accept protons released in the substitutions.

(2) Spectrophotometric determination methods:

Popa and Radulescu(17) in(1966) developed the method for photometric determination of the aromatic amines by the reaction with $NaClO_2$ in an organic solvent such as EtOH or Me_2CO. A stable violet colour appeared within 2-5 min, and measured at 533 mμ in case of : m-phenylenediamine, p-phenylenediamine, O-aminobenzoic acid, p-aminophenol, diphenylamine and benzidine. An unstable violet color was obtained for O-phenylenediamine, O- aminophenol, sulfanilic acid, and p-iodoaniline. In case of m-aminophenol, m-aminobenzoic acid, and β-naphthylamine no violet colour, but unstable red, yellow or brown colours were obtained. With O-, m- and p-nitroaniline no reaction at all was obtained.

In (1956) Jan et al(18) determined some aromatic amines photometrically in aqueous and 50% aqueous