Appendix-12 List of Summaries of Major Reports of The Chemistry Department

(1)

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MONITORING OF WATER QUALITY IN UPPER MUKUVISI RIVER IN HARARE, ZIMBABWE

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The impact of discharges from a fertilizer plant on the quality of the upper Mukuvisi River water was studied between the months of January 1989 and September 1990. Samples were collected at a point upstream from the effluent canal from the fertilizer plant, immediately downstream from the fertilizer plant and about 3 km downstream of the fertilizer plant. The water quality parameters which were monitored were temperature, pH, suspended solids, dissolved solids, conductivity, biological oxygen demand, dissolved oxygen, nitrates, phosphates, chlorides, potassium, calcium, Cu(II), Zn(II), Pb(II), Co(III), Ni(II), Cr(III), and Cr(VI). Pollution of the river waters by the fertilizer plant is evidenced by an increase in the levels of DS, NO_3^-, P-PO_4^{3-}, Cl^-, K, Ca, Cu, Fe, Zn, Pb, Co, and Cr, a drop in pH, and an increase in conductivity as the river transcended past the plant.

INTRODUCTION

Pollution of surface and underground water systems is one of the major environmental problems faced worldwide. Numerous studies, especially in developed countries, have been carried out (Baschom 1982; Canter 1979; Pardue et al. 1988). There are many reported cases of pollution of surface waters by discharges from human activities. In the United Kingdom, Woodward (1984) reported depletion of oxygen around Trent Falls in the Humber Estuary which receives industrial and sewage discharges. In Florida, Thomas et al. (1984) noticed an increase in algal blooms and heavy aquatic growth due to high concentrations of nutrients in water pumped from agricultural lands into the upper St. Johns River. In Greece, Samanidou et al. (1989) reported increases in levels of NO_3^- and NH_4^+ near agricultural areas and sewage discharge points in the Thermaikos Gulf. In Greece and also in Russia, increases in the levels of plant growth nutrients, PO_4^{3-}, NO_3^- and K^+ in the areas around the waste ejection points of fertilizer plants have been reported (Ouzounis et al. 1989; Gladushko 1979). It is therefore important to monitor the quality of the river waters that pass through potential pollution sources so as to avoid water pollution problems in the future. In Africa, limited work has been carried out on pollution of river waters (Marshall and Falcona 1973; Greichus et al. 1978; Jonnalagadda et al. 1990, 1991).

This paper presents the results of studies on the influence of fertilizer plant discharges on the quality of the receiving Mukuvisi River waters.

Mukuvisi River is one of the three major rivers supplying Lake Chivero, the main water source of the city of Harare. Lake Chivero is a large dam covering

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STUDIES ON THE LEVELS OF SULPHUR DIOXIDE, NITROGEN DIOXIDE, AMMONIA, AND HYDROGEN CHLORIDE IN AMBIENT AIR OF HARARE, ZIMBABWE

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The concentrations of sulphur dioxide, nitrogen dioxide, ammonia, and hydrogen chloride, in the ambient atmosphere of Harare were monitored over a period of one year (1988) at four selected sites - university campus, city centre, industrial area, and Msasa, an industrial site in the vicinity of a fertilizer factory. The diurnal variations varied from day to day and sulphur dioxide and nitrogen dioxide levels rose with sunlight hours, reaching peak values about midday which were sustained on some days through till late afternoon. Normally, a decreasing trend is observed by the evening. The profile of the seasonal variation in the average dayly concentrations of all the pollutants are shown for the industrial area sampling point. Sulphur dioxide levels were observed, sustained at high levels (90-120 $\mu g\ m^{-3}$) during winter extending into spring and lower levels during the rainy season. Hydrogen chloride in the winter and spring was maintained at about 40 $\mu g\ m^{-3}$. Of the four sites, the university area was found to be relatively clean with minimum and maximum daily average levels (in $\mu g\ m^{-3}$) recorded during the year, being SO_2 (2.0-52.6), NO_2 (2.0-17.2), NH_3 (1.9-38.1), and HCl (9.0-55.1). The order of increasing pollutant concentrations was the city centre, the industrial area, and the Msasa area. In the Msasa area, the pollution originated from the point source, the fertilizer factory. The minimum and maximum diurnal arthamatic means (in $\mu g\ m^{-3}$), over the year observed, were SO_2 (14.0-242.0), NO_2 (4.5-27.4), NH_3 (2.0-45.3), and HCl (14.8-77.0). The correlation plot of NH_3/SO_2 versus SO_2 gave a slope of 7.7×10^{-3} (corr. 0.69), indicating that high sulphur dioxide levels facilitate the removal of ammonia, possibly through aerosol formation from the ambient air.

INTRODUCTION

The atmosphere is a complex system from both the physical and the chemical standpoints. The variable atmospheric mixing, the variable radiation, and the nature of pollutants emitted play important roles in determining the nature and rates of chemical transformation in the troposphere. Atmospheric pollution in particular is a matter of global concern as the problem is not restricted to the boundaries of any single nation or continent.

The prime objective of a study on pollutant levels is the control of the noxious materials in atmosphere. To achieve the objective, it is essential to understand

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ENVIROMENTAL QUALITY ASSESSMENT: STUDIES ON AIR AND RAINWATER QUALITY IN ZIMBABWE

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Abstract: The quality of ambient air was assessed by monitoring the levels of four gaseous pollutants, sulphur dioxide, nitrogen dioxide, ammonia and hydrogen chloride at one urban site and two remote sites away from urban area. The rainwater in Harare area for the rainy season of 1989-90 was characterised by analysis the concentrations of sulphate, nitrate, chloride aminons and ammonium, sodium and potassium cations, in addition to the pH and conductivity of the composite monthly samples.

Key words rainwater, sulfur dioxide, nitrogen oxide, ammonia, hydrogen chloride

INTRODUCTION

Pollution is resultant of ever increasing trends of urbanisation, industrialization, indiscriminate use of resources and the poor planning. It is a global problem, which is influence the economies of both developed and developing nations in different ways. The prime objective of carrying the quality assessment is the control of noxious materials from authreopogenic activities, entering into our habitat and atmoshere. It is, therefore, extremely essential that long term measurements are performed to document the changes that are occuring in trace gas concentrations in the back ground tropophere, as these are important sensitive indicatiors of enviromental change. This is a plausible initial point in the assessement of the environment.

Most of the trace gases are precursors for the more regionally dispersed secondary pollutants such as acid deposition. Much of the sulphur and nitrogen oxides entering the atmoshere are scavenged by raindrops and converted to sulphuric and nitric acids respectively. Hydrochlolic acid resulting form hydrogen chloride emissions cause acidic precipitation studies of the composition of rainwater contribute to our knowledge of the trace gas and areosol chemistry of atmosphere and to our understanding of the biological cycles of many elements. Literative search shows that data for the southern hemisphere is still scarce (1).) A very little attention was paid to the air and rainwater quality assessment except for few studies. (2,3). In this communication the results of the studies on the air and rainwater quality in the environment, in the vicinity of Harare, the capital city of Zimbabwe are reported. Harare, the capital city of Zimbabwe with 1 million population is situated at latilude 17°s and altidute 1500 m.

The three sites identified for the study are (i) -University of Zimbabwe campus an urban site which is situated about 5 km from city centre and surrounded by thick vegetation (Fig.1). (ii) Mazoe farmlands: A site situated in farmlands, 23 km north of city of Harare - no urban activity. (iii) Mt Hampden area - 30 km from city centre and located with in the farming area. Rainwater samples were collected at Belvedere, Meteological Station situated 5 km away from city centre.

EXPERIMENTAL

Air Sampling: At the identified sites, the samples were collected for all the four gaseous pollutants at 1.5 m from ground level, simultaneously by cumulative grab sampling. Air was sucked through respective absorbing solutions, using flow regulated portable pumps with flow rates 1-2 l/min for

(42)

Bull.Chem.Soc.Ethiop.,5(2), 49-64 (1991).

RIVER POLLUTION IN DEVELOPING COUNTRIES - A CASE STUDY III: EFFECT OF INDUSTRIAL DISCHARGES ON QUALITY OF NGONG RIVER WATERS IN KENYA

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ABSTRACT. Ngong is the major river stream transversing through Kenya's major industrial belt which carries the rain runoff waters, treated and untreated industrial discharges of various types. The effect of treated and untreated industrial effluents on the quality of Ngong waters was studied over a period of one year (Nov. 1985 to Oct. 1986). To assess and characterise the quality of river waters, ten parameters, namely; temperature, pH, conductivity, biochemical oxygen demand, chemical oxygen demand, dissolved solids, suspended solids, chloride, nitrate and total phosphate were monitored at five sampling points at regular monthly intervals and during different times of a day. In addition to the ten parameters, profiles of various elements both in suspended and soluble forms in all the aquatic samples were determined using X-ray fluorescence. The overall quality status of the water was mathematically evaluated using combined data, according to the water quality index (WQI), to enable comparison of this water system with similar bodies of water internationally.

INTRODUCTION

The problem of river water pollution in the acute form in which it exists in many industrialised countries began in the 19th century with the coming of industrial revolution and resulting phenomenal growth of population [1]. In the developing countries there is an increasing awareness to minimise the levels of pollutants discharged into the environment [2]. World bodies like United Nations Environmental Programme (UNEP) are drawing the attention of Nations towards consequences of pollution. The root cause of river pollution has been man's tendency to dilute and disperse wastes than to remove at the source. With the ever increasing population levels, urbanisation and industrialisation, the environment, particularly the rivers and lakes, is considerably polluted even in the developing countries. As a result many river streams in urban areas of developing countries have been converted into heavily polluted drains.

The wastes which are discharged into waterways can be classified into three general types; domestic, industrial and agricultural. Industrial pollution, particularly the presence of organic or inorganic substances is the commonest type and is the most intractable [3].

This communication is the third in the series of river streams investigated in Kenya. The results on Nairobi and Ruiruaka rivers of Kenya have been reported earlier [4,5].

Ngong river, which flows through Kenya's major industrial belt, taking in a whole burden of all types of treated, partially treated and raw effluents, stands as an example of state of river streams in urban areas of most developing countries.

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Electrochemical reduction of folic acid reconsidered

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Abstract

Folid acid (FA) undergoes three distinct reduction steps in acidic media and a single reduction step in alkaline media. Analysis of constant potential electrolysis products by high performance liquid chromatography reveals that, in acidic medium, the first reduction step converts FA to a transient 5,8-dihydro-FA, some of which tautomerizes to 7,8-dihydro-FA, while the remainder undergoes a proton dependent non-electrochemical cleavage of the *para*-aminobenzoylglutamate side chain. Step two involves the electrochemical cleavage of the $C_{(9)}$–$N_{(10)}$ chemical bond of the 7,8-dihydro-FA while the final reduction converts the 6-methyl-7,8-dihydropterin derivative generated in step two to a 6-methyl-5,6,7,8-tetrahydropterin. Above neutrality, only a single $2e^-/2H^+$ reduction step is observed because the proton dependent tautomerization process is slow. Differential pulse, normal pulse polarography and cyclic voltammetric results indicate that reduction of FA is subject to considerable adsorption in both the acidic and alkaline media.

INTRODUCTION

The electroanalytical chemistry of folic acid (FA) and its analogues has been studied extensively [1–12] due to their biological importance and the consequent need to develop simple, reliable and sensitive methods for their determination. Based on electrochemical, in conjunction with spectroscopic methods, the postulated reduction mechanism of folic acid is that in acidic and neutral pH, it undergoes three two electron–two proton ($2e^-/2H^+$) reactions. The first step is postulated to involve the conversion of FA to 7,8-dihydro-FA via a transient 5,8-hydro-FA derivative while the second and third steps involve the electrochemical cleavage of the $C_{(9)}$–$N_{(10)}$ bond of 7,8-dihydro-FA to 6-methyl-7,8-dihydropterin

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Reversed-phase liquid chromatographic determination of cyanide as 1-benzoyl-1,2-dihydroquinaldonitrile

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(Received 19th February 1991)

Abstract

A rapid and sensitive reversed-phase liquid chromatographic (RP-LC) method for the determination of cyanide as a Reissert compound, 1-benzoyl-1,2-dihydroquinaldonitrile, is described. The derivative is formed by reaction of cyanide with quinoline and benzoyl chloride in neutral medium. RP-LC of the derivative was done on a C_{18} column with UV detection. Conditions to effect baseline resolution of the peaks were established by employing acetonitrile–phosphate buffer (pH 7) as the mobile phase. Because the derivative absorbs very strongly in the UV region, detection limits at nanogram levels were achieved. A linear dynamic range of about two orders of magnitude was demonstrated. The stability of the derivative and the effects of solvents and reaction time on derivatization were investigated and optimum detection and chromatographic conditions were established. The proposed method was applied to the determination of cyanide in wastewater from a gold mine and the results agreed well with those obtained by using a well established spectrophotometric reaction rate method.

Keywords: Liquid chromatography; Cyanide; Waters

Cyanides are used in many industries, including the metal, electroplating, paint, plastics, steel and mining industries. The high toxicity of cyanide, resulting from its inhibition of a variety of enzymes including cytochrome *c* oxidase, makes the determination of trace levels of cyanide of great importance. A variety of methods for cyanide determination have been reported, including spectrophotometric, electrochemical and chromatographic techniques.

Spectrophotometric methods are by far the most common because they are well characterized and generally sensitive, simple and practical for many laboratories. Typically, the methods are based on the conversion of cyanide to cyanogen chloride or bromide with subsequent reaction with pyridine–benzidine [1], pyridine–barbituric acid [2] or pyridine–pyrazolone [3] to form coloured compounds. Since these methods were first published, various efforts have been made to improve them in terms of stability of reagents [4–7], replacement of benzidine and increasing the sensitivity, which is generally mg l^{-1} levels. The methods suffer from serious interferences from thiocyanate in particular and other anions such as citrate, bromide, iodide thiosulphate and sulphide. Hence, prior separation of cyanide, normally by distillation, is necessary, making the procedure time consuming.

Cyanide has also been determined electrochemically by using a cyanide ion-selective electrode [8–10] and by differential-pulse polarography [11]. Despite its simplicity, the ion-selective electrode method is subject to interferences from species such as halides and sulfides.

A number of gas chromatographic (GC) methods based on derivatization have also been reported for cyanide determination. In two of these methods, cyanide was reacted with bromine water or chloroamine to form cyanogen bromide [12] or

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Effect of excess sodium on the excitation of potassium in an air-acetylene flame: a steady state kinetic model which takes into account collisional excitation

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Summary. The effects of excess Na on the ionization and excitation of K in an air-acetylene flame were studied using absorbance signal and emission signal ratios, A′/A and E′/E respectively, as probes, where A′ and E′ are the line absorbance and line emission readings in the presence of excess Na interferent, and unprimed quantities represent readings in the absence of the interferent. An emission signal enhancement which increases exponentially as the ratio of interferent to analyte increases (up to about 2000), was observed irrespective of whether measurements were made from the primary or secondary reaction zones of the flame, while a similar line absorbance signal enhancement was observed only when measurements were made from the primary reaction zone. For both line emission and line absorbance, the maximum enhancements observed are in excess of those predicted on the basis of complete suppression of ionization of analyte atoms as a result of the increased partial pressure of electrons. A steady state kinetic model is presented, which takes into account radiative recombination collisional excitation of K^+ ions and collisional charge transfer between the heavy particles, and whose predictions are consistent with the observed interference effects.

Introduction

One of the major causes of loss of spectrochemical sensitivity during flame atomic emission spectrometry is ionization of analyte atoms. This is particularly so for alkali metals. Such ionization is often minimized by the addition of another easily ionized metal, termed a radiation buffer. Enhancement of the emission signal in this way is attributed to an increase in the partial pressure of free electrons as a result of the ionization of the radiation buffer. This shifts the ionization equilibrium of the analyte in favour of neutral atoms [1, 2].

A typical example of this emission signal enhancement is the effect of alkali metals in increasing the intensity of the caesium emission signal which was studied by Poluektov and Vitkum [3]. Relative enhancements of 780, 1270, and 2260 were obtained for a 10^{-4} mol/l solution of caesium upon the addition of 1 mol/l lithium, sodium, and potassium, respectively. The measurements were made in an air-acetylene flame in which caesium, when present alone in solution, is 28.6% ionized (assuming a partial pressure of 1×10^{-6} atm) [4]. It can be shown that complete suppression of ionization would lead to an emission signal enhancement of not more than 40%. Enhancement figures obtained by Poluektov and Vitkum for caesium suggest that suppression of ionization is not the only process involved.

In this paper we report the results of our investigations into the possibility of processes other than suppression of ionization, contributing to the analyte emission signal enhancement observed upon the addition of another easily ionized metal during flame atomic emission spectrometry. For our study, we chose the potassium-sodium system, with sodium as interferent. Potassium emission signal enhancement in the presence of excess sodium was previously confirmed by Smit et al. [1], who showed that the observed emission signal enhancement was not due to changes in the physical properties of the test solution (e.g. viscosity, etc.) or to spectral interference.

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Theoretical

An atom possessing n energy levels can undergo $n(n\text{-}1)$ transitions, some of which are populating and other depopulating, between the various atomic and ionic energy levels [5]. Only fourteen of these have been found to be of significance in a flame, and comprise 8 electron collisional processes (collisional excitation, collisional decay, collisional ionization, three-body recombination, radiative recombination, autoionization, autoionization recombination, and dielectronic recombination), 3 atomic collisional processes (atom collisional ionization, atom recombination and penning ionization) and 3 radiative processes (radiative decay, absorption, and stimulated emission).

The current theory of flame atomic spectroscopy assumes local thermal equilibrium (LTE) [6], i.e. a situation where all equilibrating processes in the system are due to collisional processes and the contribution from radiative processes is so small that it can be neglected. It has however been found that the emission spectrum of analyte species, e.g. in the inductively coupled plasma, often does not conform to LTE [7]. In such cases it has been necessary to invoke partial local thermal equilibrium (p-LTE), which allows for decoupling of electrons and heavy particles, and decoupling of upper energy levels and lower energy levels [6]. The implications of p-LTE are two-fold: (a) Because of their smaller mass, the heating of electrons in a flame is much faster than transfer of energy from electrons to heavy particles, hence a two-

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The Oxidation of 3,3′-Dimethoxy Benzidine with Potassium Bromate in Acidic Solutions

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Abstract

The kinetics and mechanism of the oxidation of 3,3′-dimethoxybenzidine (oda, *o*-dianisidine) by potassium bromate in aqueous acidic medium were studied by monitoring the formation rate of the reaction product, 3,3′-dimethoxy 4,4′-diphenoquinone at 447 nm. The reaction is, first order with respect to both the substrate and oxidant, and second order with respect to H^+. The oda:bromate stoichiometric ratio is 1:1. Plausible mechanism and rate laws are proposed accounting the experimental findings. Computer simulations were done using the proposed mechanism.

Introduction

The purpose of studying the reaction between 3,3′-dimethoxybenzidine (*o*-dianisidine, oda) and acidic bromate is two-fold. First, to look into the rates and mechanism of oda oxidation in aqueous solution and, second, to explore the scope of the reaction as an indicator for analysis of trace concentrations of cations that can selectively catalyze the reaction. Literature shows that the oxidation reactions of oda have been studied using various oxidizing agents, periodate [1], hydrogen peroxide [2], *t*-butyl peroxide [3], peroxydisulfate [4], permanganate [5], chloramine-T [6], cobaltic acetate [7], manganese dioxide [5], and technetium [8,9]. The extent of oxidation depended on reaction conditions and the reagents used. Mild oxidizing agents such as *t*-butyl peroxide and ceric sulfate are reported to oxidize oda to 4,4′-diphenodiimine, while strong oxidizing reagents like permanganate and cobalt(III) acetate oxidized the diimine-intermediate further in a fast reaction [5]. Reactions involving oda have been suggested as kinetic methods for analysis of various species. Otto et al. have suggested the oda-tertiary butylperoxide reaction as a catalytic indicator reaction for analysis of V(V) in nonaqueous solvents such as acetonitrile [3]. A colorimetric assay for Mn(II) was also reported based on its catalyzing effect on photooxidation of oda [10]. The reaction between oda and acidic bromate was not previously investigated. In the present article the results of the kinetic study of the oxidation of oda with bromate in an aqueous sulfuric acid are presented and a plausible mechanism and rate laws are suggested.

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A Kinetic Study of the Oxidation of Indigo Carmine with Acidic Bromate

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The oxidation kinetics of indigo carmine (disodium 3,3'-dioxobi-indolin-2,2'-ylidene-5,5'-disulphonate) with potassium bromate have been studied in aqueous sulphuric acid, by monitoring the absorbance of indigo carmine (IC) at 610 nm. The reaction involves competitive and consecutive reaction steps—an initial slow step followed by a rapid one for depletion of IC. For the initial stages the reaction order is four-first-order with respect to IC and bromate ion and second order with H^+ ion. For the fast reaction step the studies are limited to qualitative treatment due to the complex nature of the reaction. The rate of depletion of IC increased with time and with the increase in HOBr concentration. Hypobromous acid, the reaction intermediate, may possibly compete with bromate ion for IC to give an intermediate, which is further oxidised to yield the final product, isatin-5-monosulphonic acid. The stoicheiometric ratio of IC to bromate is 3:2. The dual role of bromine ion as an inhibitor and autocatalyst in the reaction mechanism is discussed. Computer simulations were performed using the proposed mechanism. The results of the computer simulations are similar to the experimental observations.

Considerable effort has been devoted towards the understanding of the chemistry of the bromate ion in aqueous sulphuric acid and to the elucidation of the mechanism of the oscillating closed chemical systems.[1] Numerous reactions involving different organic and inorganic substrates and acidic bromate are known.[2-5]

Indigo carmine (IC) is a well known dyestuff used as a microscopic stain in biology.[6] The organic chemistry of IC and indigotin compounds has been discussed in detail by Rodd.[7] Oxidation of IC by peroxydisulphate ion in aqueous sulphuric acid[8,9] and its application as an indicator for the determination of Ag^I concentration has been reported.[10] Mn^{II} catalysed oxidation of IC by hydrogen peroxide has also been reported.[11]

Different organic substrates have been scanned for suitable reductant properties to react with acidic bromate, and which can act as a selective catalytic indicator for the determination of trace concentrations of V^V. Indigo carmine was, among the number of substrates, chosen due to its sharp absorption peak in the visible region. Investigations showed that V^V and other cations have no significant effect on the oxidation rate of IC by acidic bromate. Interestingly the reaction has two distinct stages for depletion of IC, a slow initial step followed by a very rapid one, indicating the existence of a competitive or an autocatalytic step. We now report a kinetic study of the oxidation of indigo carmine by acidic bromate.

Experimental

Reagents.—All the reagents employed were of AnalaR grade or of high purity. All the standard solutions and dilutions were made in deionised distilled water following standard procedures.

Methods.—Kinetic measurements. The reaction mixtures were stirred magnetically and the solutions were maintained at constant temperature (25 ± 0.5 °C) by circulating water from a thermostat through a water jacket surrounding the reaction vessel.

The stock solutions were mixed in the following order: requisite volume of water to make up the total volume; aqueous sulphuric acid, IC, and then the other reagents as needed. The reaction was started by the separate addition of bromate solution (at 25 ± 0.5 °C).

The kinetic studies were followed by monitoring absorbance at 610 nm, an absorption maximum for IC in acidic solution (ε $6.31 \times 10^3 M^{-1} cm^{-1}$) (Pye-Unicam SP-150 spectrophotometer). Interference from other reagents and products at this wavelength was negligible. All the kinetic data were collected in the presence of excessive concentrations of hydrogen and bromate ions, unless otherwise specified. In the concentration range of IC employed, Beer's law was valid.

Determination of $[BrO_3^- + HOBr]$.[12] Aliquots of the reaction mixture were added at intervals to a mixture of 0.1M-$HClO_4$ (10 ml) and 10% w/v potassium iodide solution (10 ml) with 10^{-6}M-molybdate catalyst. After incubation for about 30—40 min the liberated iodine was titrated with 0.002M-sodium thiosulphate solution using starch as indicator, and a correction for blanks was made. (6M-sodium thiosulphate ≡ 1M-bromate).

Determination of [HOBr].[12] For the determination of HOBr concentration alone, the same iodometric method was used, but with a slight modification. Aliquots of the reaction mixture were added to a fixed volume of aqueous NaOH in order to bring the mixture to neutral pH, this was followed by the addition of a mixture of 0.1M-acetate buffer (10 ml) and 10% KI (10 ml) solution (reaction of bromate ion with KI does not occur at the mixture pH 4.5). The solutions were incubated for 30—40 min, then the liberated iodine titrated with 0.002M-sodium thiosulphate solution and correction for the blank was made in the titre values. The concentration of HOBr was calculated using the equation 2M-sodium thiosulphate ≡ 1M-HOBr. Actual concentrations of bromate ion were determined by substracting [HOBr]/3 from the corresponding value of $[BrO_3^- + HOBr]$.

E.m.f. measurements. Electrochemical potential measurements (Pye-Unicam pH meter with expanded scale) were determined using a platinum electrode and a saturated calomel electrode, immersed in the reaction solution (25 ± 0.5 °C) and connected by an agar gel-KNO_3 salt bridge.

Stoicheiometry. The stoicheiometry of the reaction was determined using 1:1 and 1:2 molar ratios of IC and bromate ion in the presence of an excess of H^+ concentration. After 16 h and 40 h, the concentration of the reactants were determined and it was found that IC reacted with bromate ion in 3:2 ratio.

Product analysis. For the product analysis the following reactant concentrations were used H^+ 5.0M, bromate ion 0.05M, and IC 0.01M. After 24 h reaction at room temperature (about

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(10)

Autocatalytic Chlorite–Bromide Reaction

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A kinetic study was performed on the reaction $ClO_2^- + 4Br^- + 4H^+ \rightarrow Cl^- + 2Br_2 + 2H_2O$. The reaction was studied spectrophotometrically by following the production of bromine and by the redox potential traces. The reaction was found to proceed in two distinct pathways, with one of them catalyzed by the product bromine, and suppressed by the reactant bromide. At room temperatures (25 ± 0.1 °C) and ionic strength 0.5 M ($LiClO_4$) the rate expression is as follows: $^1/_2\, d[Br_2]/dt = k_1[ClO_2^-][H^+][Br^-] + k_2[ClO_2^-]\,[Br_2]/[Br^-]$, with $k_1 = (1.39 \pm 0.05) \times 10^{-1}\ M^{-2}\ s^{-1}$. At high bromide concentrations the first term predominates, and the value of k_1 was evaluated in this environment. At low bromide concentrations the reaction behaves like a typical clock reaction with an induction period which precedes a sudden and very rapid production of bromine which occurs in unison with a proportional rapid consumption of bromide.

Introduction

Very few kinetic studies have been performed on oxyhalogen–halide reactions. About 20 years ago, studies were carried out on the chlorite–iodide reaction with interesting results.[1-3] At certain conditions autocatalysis was discovered in this system, in which the product, iodine, catalyzed the reaction.[2,3] Although it can be superseded by complex feedback loops,[4] autocatalysis has been found to be a constant feature of all known chemical oscillators.[5] Indeed, the chlorite–iodide reaction has been recently found to be involved in a number of systematically designed chemical oscillators.[6-8] Chlorite has also been involved in other oscillators in both flow reactors and batch which do not involve iodide.[8-11] It is also remarkable to note that all known chemical oscillators are found to involve at least one oxyhalogen species.

In this paper, we report the results of a kinetic study we have done on the chlorite–bromide reaction. Our interest in this system was roused by the fact that iodide and bromide reactions are usually similar, and that very slow oscillations had already been observed in the system.[12]

Our study is purely kinetic. The establishment of oscillations in a flow reactor with the chlorite–bromide reaction would generally suggest nonlinearity in the reaction, based upon the expected preconditions for chemical instability. Availability of the kinetic parameters that control the chlorite–bromide reaction will enhance a better understanding of the origin of the oscillations. We hope

(1) Indelli, A. *J. Phys. Chem.* 1964, *68*, 3027–3031.
(2) Kern, D. M.; Kim, C.-H. *J. Am. Chem. Soc.* 1965, *87*, 5309–5313.
(3) De Meeus, J.; Sigalla, J. *J. Chim. Phys. Phys.-Chim. Biol.* 1966, *63*, 453–459.
(4) (a) Boissonade, J.; De Kepper, P. *J. Phys. Chem.* 1980, *84*, 501–506. (b) Higgins, J. *Ind. Eng. Chem.* 1967, *59*, 19.
(5) (a) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* 1981, *103*, 6121–6127. (b) Franck, U. F. *Symp. Faraday Soc.* 1975, *No. 9*, 137–149.
(6) Dateo, C. E.; Orban, M.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* 1982, *104*, 504–509.
(7) De Kepper, P.; Epstein, I. R.; Kustin, K.; Orban, M. *J. Phys. Chem.* 1982, *86*, 170, 171.
(8) Orban, M.; Dateo, C.; De Kepper, P.; Epstein, I. R. *J. Am. Chem. Soc.* 1982, *104*, 5911–5918.
(9) Orban, M.; Epstein, I. R. *J. Phys. Chem.* 1983, *87*, 3212–3219.
(10) Orban, M.; De Kepper, P.; Epstein, I. R. *J. Phys. Chem.* 1982, *86*, 431–433.
(11) Orban, M.; De Kepper, P.; Epstein, I. R. *Nature (London)* 1981, *292*, 431–433.
(12) Alamgir, M.; Epstein, I. R. *J. Am. Chem. Soc.*, in press.

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Acridine orange-bromate reaction. A kinetic method for the analysis of V(V)

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Introduction

Numerous kinetic methods have been described for the analysis of low concentrations of vanadium, utilising its efficiency to catalyse redox reactions, employing various organic substrates and oxidising agents [1–3]. In this communication, the scope of the acidic bromate-acridine orange (AO) reaction as a catalytic indicator reaction for the determination of V(V) is reported.

Experimental

Reagents

All the reagents employed were of Analar grade or of high purity. All the standard solutions and dilutions were made in deionised distilled water following standard procedures. A standard solution of 0.1 mol/l V(V) was prepared by dissolving the requisite amount of ammonium vanadate in 0.1 mol/l sulphuric acid.

Methods

Kinetic studies. All the kinetic studies were conducted at 25 ± 0.5°C by circulating water from a thermostat through a water jacket surrounding the reaction vessel. The reaction mixtures were stirred magnetically. In all the experiments the requisite volumes of stock solutions of dilute sulphuric acid and AO were thermostated, together with the other required reagents. Measurements were done on Shimadzu UV-Visible Spectrophotometer at 492 nm. No interference from the reactants or products was observed at this wavelength. Beer's law was obeyed in the concentration range of AO examined.

Procedure

To a freshly prepared aqueous solution of acridine orange (2.5 ml, 10^{-3} mol/l), water (0.5 ml) and sulphuric acid (8.0 ml, 5.0 mol/l) were added, followed by 5.0 ml of sample solution containing V(V) less than 5.0×10^{-6} g/ml. The reaction was started by the addition of bromate solution (4.0 ml, 0.02 mol/l) to the thermostated mixture (25°C). The time for the absorbance (at 492 nm) to reach the requisite value was recorded for each run.

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Results and discussion

The reaction of acridine orange with bromate in acidic solution involves complex kinetics with an initial fast reaction leading to equilibrium, followed by a rapid depletion step due to attack by the reaction intermediate HOBr on AO. The reaction is sensitive to the presence of V(V). Increase in initial concentration of V(V) increased the overall reaction rate and decreased the induction time (I_t), the time for transition to the rapid autocatalysed reaction step.

Experiments were carried out with fixed initial concentrations of H^+, bromate and acridine orange but using different concentrations for standard solutions of V(V). Figure 1 shows the effect of V(V) concentration on the kinetic curve. The variable time method was adopted for plotting the calibration curves. The plots of reciprocal of I_t versus [V(V)]

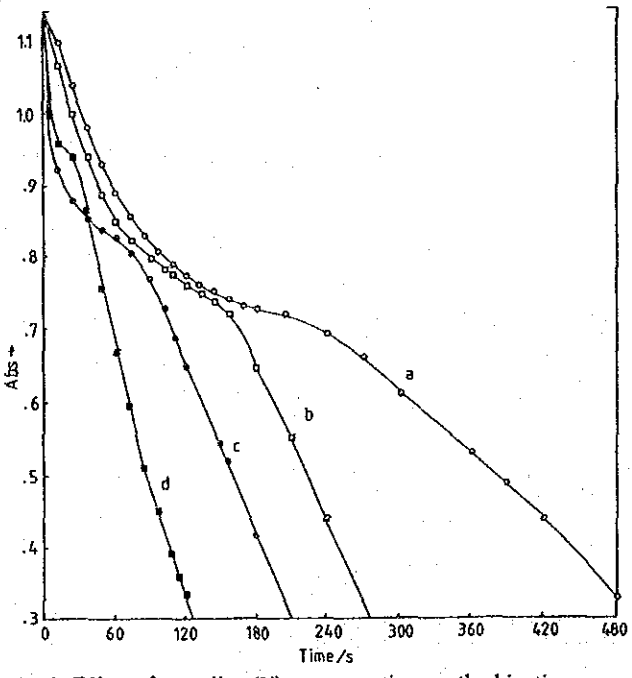

Fig. 1. *Effect of vanadium(V) concentration on the kinetic curve.* Absorbance at 492 nm (*Abs*) versus time plots. [H^+] 2.0 mol/l, [bromate] 4.0×10^{-3} mol/l, [AO] 80×10^{-5} mol/l. Curve *a* no vanadium; curve *b* [V(V)] 1.0×10^{-5} mol/l; curve *c* [V(V)] 2.0×10^{-5} mol/l; curve *d* [V(V)] 10.0×10^{-5} mol/l

(12)

A Kinetic Approach for the Mechanism of Malachite Green-Peroxydisulphate Reaction in Aqueous Solution

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Abstract

The oxidation kinetics of malachite green (MG) with peroxydisulphate ion (PDS) were investigated by monitoring the absorbance change at 618 nm, in aqueous solutions under buffered and unbuffered conditions. Under both conditions, the reaction had first order dependence on reductant and a fractional order (one half) dependence on the oxidant. The stoichiometric ratio between MG and PDS was 1:2. The reaction had a negative salt effect. Reaction rates were enhanced under both high or low pH relative to neutral conditions. A plausible mechanism is proposed.

Introduction

The peroxydisulphate ion is a powerful two-electron oxidizing agent. Using its immense attacking capacity in acidic, neutral, and alkaline conditions, oxidation reactions of the inorganic and organic substrates have been extensively studied and findings have been reviewed by House [1], Wilmarth et al. [2], and Wilson [3]. Oxidation of various substrates by peroxydisulphate ion (PDS) is known to occur through several schemes: (i) a two-electron transfer by the direct reaction between the reductant and oxidant [4]; (ii) two successive reaction steps of the one-electron transfer from the reductants [2]; (iii) a reaction initiated by the thermal decomposition of peroxydisulphate, with no direct reaction between the reactants, (i.e., through a reaction between reducing substrate and the sulphate radical ion [5]). Beyond elucidation of oxidation reaction mechanisms, the kinetic data of the reactions involving PDS have been successfully used in designing catalytic rate methods for analysis of trace concentrations of Ag(I) [6, 7] Cu(II) [8], and Au(II) [9] by using their selective catalytic efficiencies on specific indicator reactions. Inhibitory effects on silver ion catalyzed peroxydisulphate reaction kinetics have been used in methods for determination of trace amounts of cysteine [10], iodine, bromide, thiocyanate [11], and Co(II) [12] ions.

Malachite green (MG), an intensely-colored dye which is used as a biological strain to differentiate between various bacteria, has a sharp absorption peak in the visible region. Oxidation reactions of MG by Mn(III) diphosphate complex [13], Cr(IV) [14], and periodate [15] have been reported. The MG-periodate reaction, which is catalyzed by Mn(II) has been suggested as ki-

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A Kinetic Study of the Reduction of Toluidine Blue with Thiourea in Acidic Solution

(13)

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Abstract

A detailed kinetic study of the reaction of toluidine blue (tolonium chloride) (TB^+Cl^-) with thiourea (TU) in aqueous hydrochloric acid solution is reported. The reaction was first order with respect to toluidine blue and the reductant and second order with respect to $[H^+]$. Thiourea had a 2:1 stoichiometric ratio with TB^+. Toluidine blue was reduced to a colorless base in two one-electron reduction steps and TU was oxidized to thioformamidinium ion, which dimerized rapidly to give stable dithioformamidinium ion. The energy parameters obtained for TB^+-TU reaction were mean energy of activation (Ea') = 26.7 ± 2.4 kJ M^{-1}; enthalpy of activation ($\Delta H^{\neq}$) = 24.2 kJ M^{-1}; frequency factor (A) = 1.04×10^4 M^{-3} s^{-1}; and entropy of activation ($\Delta S^{\neq}$) = −176.35 J M^{-1} s^{-1}.

Introduction

Toluidine blue, a phenothiazine blue dye, is normally used as a staining and sensitizing agent in biological reactions [1]. The phenothiazine dyes are also used as polymerization inhibitors and complexing agents [2]. Furthermore, the scope of redox reactions of phenothiazine dyes may be exploited for the storage of solar energy using photo galvanic cells [3]. Burger and Field reported an uncatalyzed oscillatory reaction between methylene blue and sulfide [4]. The uncatalyzed and V(V) catalyzed reaction between methylene blue and acidic bromate has been reported [5]. A number of reduction reactions [6] and analytical methods [7,8] using methylene blue and various chemical species were also studied. Studies on pulse radiolytic reduction of toluidine blue [8] and kinetic determination of Se using its catalytic efficiency on reduction of TB by sulphide has been reported [9]. The low toxicity and easy water solubility of toluidine blue with an intense absorption peak in the visible region (λ_{max} 626 nm) makes it a suitable substrate to monitor its depletion kinetics using other reactants. In our studies, to explore their scope as a catalytic indicator reactions, the reactions of toluidine blue with thiourea in acidic solutions have been investigated. Similar studies have not been reported earlier. Of the various cations tried, no cation possessing selective catalyzing efficiency for the TB^+-thiourea reaction was found.

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The Stereochemistry of Tri-n-butyltin Hydride Reductions in the Preparation of Ring A Desoxygibberellins

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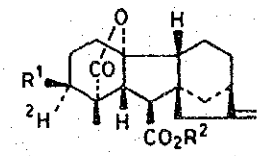
The hydrogenolysis of gibberellin 1- and 3-chlorides with tri-n-butyltin hydride has been shown by deuterium labelling combined with ^1H and ^2H n.m.r. analysis, to proceed with the introduction of the label from the less hindered β-face of the molecule. The hydrogenolysis reaction when applied to the preparation of 3-desoxygibberellins in the C-20 series, proceeds most satisfactorily with the thiocarbonylimidazole derivatives of gibberellins A_{13} and A_{14} methyl esters to afford the methyl esters of gibberellins A_{28} and A_{12} respectively.

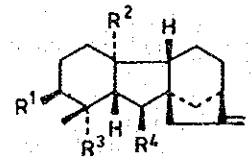
The hydrogenolysis of alkyl halides with tri-n-butyltin hydride[1] has proved to be a useful reaction in the partial synthesis of gibberellin plant hormones.[2,3] Despite the sparsity of stereochemical information on these reductions, the availability of tri-n-butyltin deuteride affords a means of labelling these hormones for metabolic studies. Beale *et al.* have examined the stereochemistry of reduction in the gibberellin series by a combination of chemical and metabolic studies.[3] [3α-^{2}H]Gibberellin A_9 (1) was prepared by the reduction of 3β-chloro[3α-^{2}H]gibberellin A_9 methyl ester (2) with tri-n-butyltin hydride and hydrolysis. It was shown to be hydroxylated by a cell-free enzyme preparation from *Cucurbita maxima* to afford [3α-^{2}H]gibberellin A_4 (3). On the assumption that this enzymatic hydroxylation takes place with retention of configuration, it followed that the reduction with tri-n-butyltin hydride had also taken place with retention of configuration. We have used tri-n-butyltin deuteride to introduce labels at C-1, C-3, and C-13 in the gibberellins.[4] In this paper we present our evidence for the stereochemistry of these reductions based on n.m.r. studies together with applications of the reagent in preparing 3-desoxygibberellins from their more readily accessible 3-hydroxy counterparts.

In studies on the conversion of gibberellin A_{13} trimethyl ester (4) into δ-lactones related to gibberellin A_{15}, Cross observed[5] long-range couplings on both the 19-H proton n.m.r. resonances of the lactone (8) and suggested that these involved coupling to the 3β- and 5β-protons. We have utilized the long-range coupling between a 19-H and 5β-H resonance in stereochemical studies involving reactions at C-19.[6] In a saturated desoxy ring A in which the 3-H resonances lie within the methylene envelope, this long-range coupling provides a probe for the stereochemistry of a proton (deuteron) at C-3. This coupled with ^{2}H n.m.r. studies, formed the basis of our stereochemical analysis.

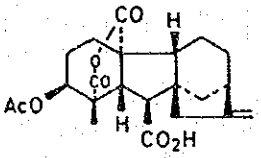
The reduction of gibberellin A_{13} trimethyl ester (4) and its relatives with lithium aluminium hydride has been described on a number of occasions.[5,7,8] The tetraol (5) is obtained under vigorous conditions in refluxing dioxane.[7] Under controlled conditions (tetrahydrofuran, −55 °C) reduction of the acetoxy anhydride (7) gave the 3-hydroxy 20-19-lactone (9).[5] In boiling ether reduction of gibberellin A_{13} trimethyl ester gave two products which were isolated as their acetates (6) and (10).[8] Thus the C-20 ester is much less reactive than the C-7 and C-19 esters. In our hands reduction of the trimethyl ester in tetrahydrofuran gave the dihydroxy-lactone (11). Treatment of the dihydroxy lactone (11) with triphenylphosphine–carbon tetrachloride gave the 3α,7-dichloride (12). The stereochemistry of the chloride was based on the following evidence. Spin-decoupling experiments based on irradiation at δ 4.64 and 4.16 (19-H) and δ 3.76 and 3.64 (7-H) and δ 1.84 (5-H) established the relationships and assignments shown in Figure 1(a). In particular, the presence of a long-range coupling (J 1.3 Hz) to one of the 19-H protons (δ 4.16) together with an axial,equatorial (6 Hz) coupling to a multiplet at δ 2.3 and an axial,axial coupling (12.5 Hz) to a multiplet at δ 1.95, established that 3-H was β and axial. Furthermore, whilst the 5-H signal (δ 1.84) appeared at higher field than in the parent dihydroxylactone (δ 2.03), the *pro-H* 19-H was shifted to lower field (δ 3.97 ⟶ 4.64) thus implying that the C-3 halogen had the α-configuration.



(1) $R^1 = R^2 = H$
(2) $R^1 = Cl, R^2 = Me$
(3) $R^1 = OH, R^2 = H$



(4) $R^1 = OH, R^2 = R^3 = R^4 = CO_2Me$
(5) $R^1 = OH, R^2 = R^3 = R^4 = CH_2OH$
(6) $R^1 = OAc, R^2 = CO_2Me$, $R^3 = R^4 = CH_2OAc$



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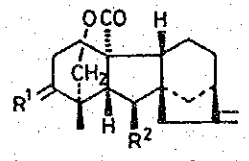

(8) R^1 = α-OH, β-H, $R^2 = CO_2Me$
(9) R^1 = β-OH, α-H, $R^2 = CO_2H$
(10) R^1 = β-OAc, α-H, $R^2 = CH_2OAc$
(11) R^1 = β-OH, α-H, $R^2 = CH_2OH$
(12) R^1 = α-Cl, β-H, $R^2 = CH_2Cl$
(13) $R^1 = H_2$, $R^2 = CH_3$

Reduction of the dichloride with tri-n-butyltin hydride gave the lactone (13). Spin-decoupling experiments based on irradiations at δ 1.00 (7-H), 1.40 (3-H), 1.70 (3-H), and 4.05 and 4.30 (19-H) established the assignments and coupling pattern shown in Figure 1(b). In this case the axial 3β-H proton (δ 1.40) showed a long-range coupling (J 2.3 Hz) to the *pro-S* 19-H (δ 4.30) and a geminal coupling (J 14 Hz) to the equatorial 3α-H (δ 1.71). Repetition of the reduction with tri-n-butyltin deuteride

Substitution Reactions of the 3-Epimeric Methanesulphonates of Methyl Gibberellate

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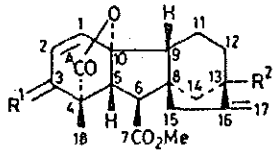
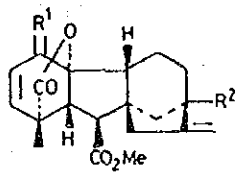
Whereas displacement of the 3β-(axial)-methylsulphonyloxy group from methyl gibberellate with lithium chloride or buffered aqueous acetone proceeds predominantly with *syn* rearrangement to afford the 1β-chloro- or 1β-hydroxy-gibberellin, the corresponding 3α-(equatorial) epimer reacts with simple inversion of configuration. This affords on the one hand a facile route to the 1-hydroxygibberellins and, on the other, a means of labelling gibberellins at C-3.

The *stereochemistry* of allylic displacement reactions has recently attracted considerable attention.[1,2] The presence of a lactone ring across the α-face of ring A of methyl gibberellate (1) ensures that this is a rigid system in which the stereochemistry of substituents at C-1 and C-3 are well-defined. The ^{1}H n.m.r. signals of the Δ^1- and Δ^2-olefinic protons are quite different whilst it is possible to distinguish between axial and equatorial electronegative substituents at C-1 and C-3 by the effect of the diaxial transannular interactions with 5β-H on its chemical shift (see for example refs. 3—7). This is particularly the case where epimers can be compared. Hence methyl gibberellate provides a suitable substrate for the study of the stereochemistry of allylic substitution reactions. The allylic displacement of the 3β-axial hydroxy group of methyl gibberellate by halides has been reported on a number of occasions.[3-5] The allylic substitution proceeds with *syn* stereochemistry and, depending upon the reagent, it is accompanied by varying amounts of nucleophilic substitution at C-3 with inversion of configuration. In their work on the reconstruction of ring A of methyl gibberellate, Corey *et al.* described[3] the reaction of the 3β-toluene-*p*-sulphonate with lithium bromide in HMPA which gave a mixture of 1α- and 1β-bromo compounds. It was later suggested[5] that these were the 1β- and 3α-bromides. Reaction of methyl gibberellate with fluoroamine and lithium chloride gave[4] entirely 1β-chloro compounds differing in the nature of the 13-substituents. MacMillan has described[5] the chlorination of methyl gibberellate with toluene-*p*-sulphonyl chloride and lithium chloride which gave predominantly the 3α-chloride (63%) with only a little (11%) 1β-chloride. In connection with gibberellin partial synthesis,[6] we contrasted[7] the reaction of methyl gibberellate (1) and triphenylphosphine–carbon tetrachloride with that of its 3-epimer (2). This reaction gave products derived from both simple bimolecular substitution and from rearrangement. In the rearrangement reaction, the 3β-(axial) alcohol gave the *syn* 1β-chloro compounds whilst the 3α-(equatorial) epimer gave the same *anti* 1β-chloro products. This result conformed with the analysis of Toromanoff[8] who suggested that when a leaving group is quasi-axial the allylic substitution product would possess the *syn* stereochemistry whilst its quasi-equatorial epimer would afford the *anti*-product. In an effort to extend these stereochemical studies, we have examined the displacement of the 3-methanesulphonates derived from methyl gibberellate and its 3-epimer with chloride and hydroxide ions. Our results, which differ in some respects from those reported earlier with the fluoroamine–lithium chloride and toluene-*p*-sulphonyl chloride–lithium chloride systems, form the subject of this paper.

Treatment of methyl gibberellate (1) with methanesulphonyl chloride in pyridine gave the 3β,13-dimethanesulphonate (3) and the 1β-chloro-13-methanesulphonate (17) with which it co-crystallized. Shorter reaction times gave the 3β-monomethanesulphonate (16).[9] In view of the nature of the investigations alternative preparations were tried. Although the methanesulphonyl chloride–sulphur dioxide system was not successful, methanesulphonic anhydride in pyridine gave the pure dimethanesulphonate (3). The 3α,13-dimethanesulphonate (4) was obtained from the 3α,13-diol (2) using methanesulphonyl chloride. Unless they were purified rigorously both dimethanesulphonates decomposed easily. Gibberellin A_7 methyl ester gave a 3-methanesulphonate on brief treatment with methanesulphonyl chloride.



	R^1	R^2
(1)	α-H,β-OH	OH
(2)	α-OH,β-H	OH
(3)	α-H,β-OMs	OMs
(4)	α-OMs,β-H	OMs
(5)	αCl,β-H	OMs
(6)	αH,β-Cl	OMs
(7)	α-OMs,β-^{2}H	OMs
(8)	α-OH,β-H	OMs
(9)	α-H,β-OTs	OH
(10)	α-OTs,β-H	OH
(11)	α-H,β-OH	OMs
(12)	α-H,β-OH	H
(13)	α-OH,β-^{2}H	OH
(14)	α-OH,β-H	H
(15)	α-H,β-OMs	H
(16)	α-H,β-OMs	OH



	R^1	R^2
(17)	α-H,β-Cl	OMs
(18)	α-H,β-OH	OMs
(19)	α-H,β-OH	OH
(20)	=O	OMs
(21)	α-OH,β-H	OMs
(22)	α-OH,β-H	OH
(23)	α-OH,β-H	H
(24)	α-H,β-OH	H

When the 3β,13-dimethanesulphonate (3) was treated with lithium chloride in pyridine, two products were obtained. The first of these (56%) was the 1β-chloro-13-methanesulphonate (17). In accordance with this structural assignment, the ^{1}H n.m.r. signal at δ 4.53 (d, *J* 3 Hz, 1-H) was coupled to the 2-H signal (δ 5.95, dd, *J* 3 and 10 Hz) which in turn was coupled to the 3-H signal (δ 5.86, d, *J* 10 Hz). The magnitude (3 Hz) of the 1-H,2-H coupling constant together with the position of the 2-H signal and the 5-H signal (δ 3.13) were indicative of a 1β- rather than a 1α-chloro compound (1β,13-dichloride, $J_{1,2}$ 3 Hz; 2-H, δ 5.95; 5-H, δ 3.10; 1α,13-dichloride, $J_{1,2}$ 3.5 Hz; 2-H, δ 5.84; 5-H, δ 2.98).[5,7] The second minor product (15%) was the 3α-chloro-13-methanesulphonate (5) in which the 3-H signal appeared as a multiplet (δ 4.63) whilst the 2-H resonance was at δ 5.85 (*J* 2 and 9 Hz) and the 1-H resonance appeared at δ 6.22 (*J* 2 and 9 Hz), a separation which is characteristic of the Δ^1- rather than the

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Electrochemical reduction of folic acid reconsidered

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Abstract

Folid acid (FA) undergoes three distinct reduction steps in acidic media and a single reduction step in alkaline media. Analysis of constant potential electrolysis products by high performance liquid chromatography reveals that, in acidic medium, the first reduction step converts FA to a transient 5,8-dihydro-FA, some of which tautomerizes to 7,8-dihydro-FA, while the remainder undergoes a proton dependent non-electrochemical cleavage of the *para*-aminobenzoylglutamate side chain. Step two involves the electrochemical cleavage of the $C_{(9)}$–$N_{(10)}$ chemical bond of the 7,8-dihydro-FA while the final reduction converts the 6-methyl-7,8-dihydropterin derivative generated in step two to a 6-methyl-5,6,7,8-tetrahydropterin. Above neutrality, only a single $2e^-/2H^+$ reduction step is observed because the proton dependent tautomerization process is slow. Differential pulse, normal pulse polarography and cyclic voltammetric results indicate that reduction of FA is subject to considerable adsorption in both the acidic and alkaline media.

INTRODUCTION

The electroanalytical chemistry of folic acid (FA) and its analogues has been studied extensively [1–12] due to their biological importance and the consequent need to develop simple, reliable and sensitive methods for their determination. Based on electrochemical, in conjunction with spectroscopic methods, the postulated reduction mechanism of folic acid is that in acidic and neutral pH, it undergoes three two electron–two proton ($2e^-/2H^+$) reactions. The first step is postulated to involve the conversion of FA to 7,8-dihydro-FA via a transient 5,8-hydro-FA derivative while the second and third steps involve the electrochemical cleavage of the $C_{(9)}$–$N_{(10)}$ bond of 7,8-dihydro-FA to 6-methyl-7,8-dihydropterin

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Triclocarban and Cloflucarban: I. Gas-Liquid Chromatography of Triclocarban, Cloflucarban and Related Anilines after Silylation

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A method is presented for the simultaneous determination of Triclocarban (N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl)urea, [101-20-2] Cloflucarban (N-(4-chlorophenyl)-N'-[4-chloro-3-(trifluoromethyl)phenyl]urea, [369-77-7]) and the related anilines, 4-chloroaniline, 3,4-dichloroaniline and 4-chloro-3-trifluoromethyl aniline.* Temperature programmed gas chromatography, after preparing trimethylsilyl derivatives is employed, using MSTFA (N-methyl-N-trimethyl-silyl trifluoroacetamide) as the derivatizing agent and a column with Dexsil 400 as the stationary phase. On a glass column quantitative results are obtained and linear calibration plots are obtained using phenanthrene as an internal standard, for 20-400 ng Triclocarban with a flame-ionization detector. Well-resolved gas chromatograms are obtained for the several compounds.

*KEY WORDS: Triclocarban, Cloflucarban, antimicrobial agents, gas chromatography.

INTRODUCTION

Triclocarban, (N-4(-chlorophenyl)-N'-(3,4,-dichlorophenyl)-urea [101-20-2]), and Cloflucarban, (N-(4-chlorophenyl)-N'-[4-chloro-3-(trifluoromethyl)-phenyl]-urea [369–77–7]), are antimicrobial agents in common use in medicated "deodorant" soap and healthcare personnel hand-wash, either singly or in combination. The use of the antimicrobial agents

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Synthesis of the 3′-Terminal Half of Yeast Alanine Transfer Ribonucleic Acid ($tRNA^{Ala}$) by the Phosphotriester Approach in Solution. Part 1. Preparation of the Nucleoside Building Blocks

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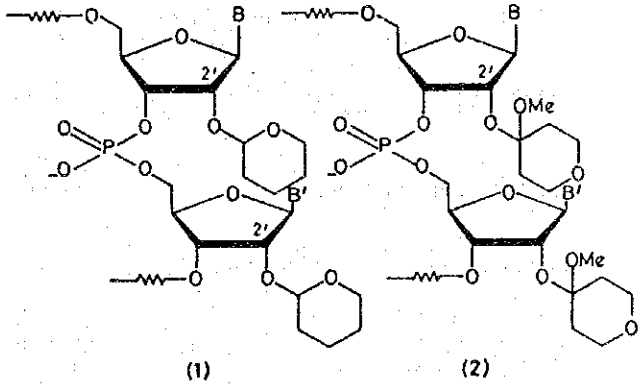
Adenosine and cytidine are converted into their 6-*N*- and 4-*N*-(4-t-butylbenzoyl) derivatives [(**12**) and (**13b**), respectively] which are then converted into the corresponding 2′-*O*-(4-methoxytetrahydropyran-4-yl) [(**21**; B = **5b**) and (**21**; B = **6b**), respectively] and 5′-*O*-[2-(dibromomethyl)benzoyl]-2′-*O*-(4-methoxytetrahydropyran-4-yl) derivatives [(**35**; B = **5b**) and (**35**; B = **6b**), respectively]. The conversion of (**12**) into its 2′,3′-*O*-methoxymethylene derivative (**24**) is also described. Guanosine is converted, by two routes, into its 6-*O*-(3-chlorophenyl)-2-*N*-phenylacetyl derivative (**16a**), and the latter compound is converted into its 5′-*O*-[2-(dibromomethyl)benzoyl]-2′-*O*-(4-methoxytetrahydropyran-4-yl) and 5′-*O*-(9-phenylxanthen-9-yl)-2′-*O*-(4-methoxytetrahydropyran-4-yl) derivatives [(**35**; B = **9b**) and (**26**), respectively]. The preparation of 2′-*O*-(4-methoxytetrahydropyran-4-yl)-4-*O*-(2,4-dimethylphenyl)uridine (**18**) from 2′-*O*-(4-methoxytetrahydropyran-4-yl)uridine (**17a**) and its conversion to its 5′-*O*-[2-(dibromomethyl)benzoyl]derivative (**35**; B = **10**) are described. 5-Methyluridine (**19**; B = **27**), pseudouridine (**19**; B = **28a**) and inosine (**19**; B = **29**) are converted into their 2′-*O*-(4-methoxytetrahydropyran-4-yl) derivatives (**21**; B = **27**, **28a**, and **29**, respectively); (**21**; B = **27**) is further converted into its 4-*O*-phenyl derivative (**30**), (**21**; B = **28a**) is further converted into its 1-*N*-(4-bromobenzenesulphonyl) and 5′-*O*-[2-(dibromomethyl)benzoyl]-1-*N*-(4-bromobenzenesulphonyl) derivatives [(**32**) and (**35**; B = **28b**), respectively], and (**21**; B = **29**) is further converted into its 1-*N*-pivaloyloxymethyl- and 1-*N*-methyl derivatives [(**33a**) and (**33b**), respectively]. The N^1,N^1,N^3,N^3-tetramethylguanidinium *E*-2-nitrobenzaldoximate-promoted removal of *O*-aryl protecting groups from the 2′-*O*-(4-methoxytetrahydropyran-4-yl) derivatives of 6-*O*-(3-chlorophenyl)-2-*N*-phenylacetylguanosine, 4-*O*-(2,4-dimethylphenyl)uridine, 5-methyl-4-*O*-phenyluridine and 1-*N*-(4-bromobenzenesulphonyl)-5-β-D-ribofuranosyluracil [(**21**; B = **9b**), (**18**), (**30**), and (**32**), respectively], and the ammonia-promoted removal of the 1-*N*-pivaloyloxymethyl group from (**33a**) are described. Finally, the synthesis of 2-(isopropylthiomethoxymethyl)benzoic acid [Ptmt acid, (**40**)], the conversion of (**18**) and (**21**; B = **5b**) into their 5′-*O*-Ptmt derivatives [(**41a**) and (**41b**)], and the two-step procedure for the removal of the Ptmt protecting group are described.

In oligo- and poly-ribonucleotide synthesis, it is of crucial importance[1] that all the 2′-hydroxy functions should be suitably protected throughout the assembly of the desired sequences, and then released in the very last unblocking step under conditions that do not lead to cleavage or migration of the 3′ ⟶ 5′-internucleotide linkages. A number of years ago, we found[1] that the tetrahydropyranyl [as in (**1**)] and more particularly the custom-designed achiral methoxytetrahydropyranyl[2] [Mthp, as in (**2**)] groups were especially suitable for 2′-protection, and indeed formed the opinion that they were the protecting groups of choice in oligoribonucleotide synthesis in solution. The results of subsequent studies have not caused us to revise this opinion.

We have, for a long time,[3] been particularly interested in the methodology of oligoribonucleotide synthesis and, in more recent years, have evaluated the usefulness of our methods in terms of their suitability for the synthesis of sequences of yeast alanine transfer ribonucleic acid (yeast $tRNA^{Ala}$, Figure 1). No really significant progress was made in our studies prior to the development of the phosphotriester approach with aryl[3,4] [especially 2-chlorophenyl, as in (**3**)] protecting groups for the internucleotide linkages. Significant progress also depended on the introduction of 'protected' protecting groups such as 2-



(**1**) (**2**)

(dibromomethyl)benzoyl[5] [Dbmb, as in (**3**)]. The latter protecting group can be removed from 5′-terminal hydroxy functions of fully-protected oligoribonucleotides [as in the conversion of (**3**) into (**4**), Scheme 1] under very mildly basic conditions that do not lead to concomitant unblocking of the internucleotide linkages. Following these developments, we were able to

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A COUMARIN GLUCOSIDE FROM *XEROMPHIS OBOVATA**

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Key Word Index—*Xeromphis obovata*; Rubiaceae; coumarins; iridoids; xeroboside.

Abstract—From root bark of *Xeromphis obovata* three coumarins have been isolated: scopoletin, its 7-β-D-glucopyranoside (scopolin) and the new β-D-apiosyl-(1″→6′)-β-D-glucopyranoside of scopoletin, named xeroboside. Also two iridoids, deacetylasperulosidic acid methyl ester and gardenoside, have been isolated and identified as the corresponding acetyl derivatives.

INTRODUCTION

Xeromphis obovata (Hochst) Keay [2] is an arboreal plant of central and southern Africa utilized in traditional medicine. A decoction of the powdered root is applied directly on melanomas while the infusion is administered by mouth as an emetic and to relieve fever, nausea, general coughs, toothache, pains during pregnancy, dizziness, menorrhagia and depressed fontanelle. The pain relief is common to another *Xeromphis* species, *X. spinosa* (Thumb.) Keay [3]. Glucosides of oleanolic acid [4, 5] have been isolated from its pulp and leaves which are used as a piscicide [3].

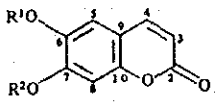
RESULTS AND DISCUSSION

CCD of the methanolic extract of root bark of *X. obovata* from Zimbabwe (vernacular name, ingwaqela) gave scopoletin 1, scopolin (7-β-D-glucopyranoside of scopoletin) (2) [6], a new diglucocoumarin, named xeroboside (3), and a mixture of two iridoids. The latter was easily resolved through the corresponding acetyl derivatives upon previous verification by NMR of the absence of any acetyl groups. The three acetyl iridoids obtained were identified as deacetylasperulosidic acid methyl ester hexaacetate [7], gardenoside hexaacetate and pentaacetate [8].

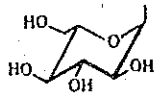
Xeroboside, 3, has the molecular formula $C_{21}H_{26}O_{13}$. Its UV spectrum is similar to that of scopoletin [λ_{max}^{EtOH} nm (log ε): 338 (3.93), 287(3.75), 258 and 248 sh, 226 (4.22)]with a slight hypochromic effect. The ^{1}H NMR spectrum (DMSO-d_6) confirmed the presence of the scopoletin moiety and showed the presence of two anomeric protons (δ5.10, *d*, J=6 Hz, and 4.80, *d*, J=2 Hz) instead of one as in scopolin (δ5.10). On enzymatic hydrolysis with β-glucosidase, xeroboside gave glucose and apiose besides scopoletin. Both positive and negative ion FAB-mass spectra confirmed the M_r ([M]$^+$ = m/z 486) and showed the loss of a pentose unit (132 mu) followed by a hexose (162 mu).

In the ^{13}C NMR spectra scopolin and xeroboside the resonances of the glucose unit are practically identical except for that of C-6′ which is at δ67.5 in the latter and δ60.7 in the former. This downfield shift for C-6 in 3 can be related to the attachment of the apiose unit. The downfield shifted C-1″ of apiose (δ109.4) confirms the β configuration of the anomeric linkage [9] cleaved by β-glucosidase albeit with difficulty.

The ^{1}H NMR spectrum of the pentaacetylxeroboside 4 confirms the 1″→6′ linkage of the apiose to the glucose unit. In fact whereas the resonances of H-2′, H-3′ and H-4′ of the glucose are shifted downfield by acetylation, the resonances of H_2-6′ remain upfield (δ3.70 and 3.84, AB part of the ABX system, X part at δ3.55, H-5′) as well as that of the AB system of the methylene group, H_2-4″, of apiose (δ3.82 and 3.98, J_{gem}=11 Hz). The other two AB systems of apiose are at δ4.22 and 4.34 (J_{gem}=11.5 Hz, H_2-5″) and at δ4.93 and 4.98 (J=2 Hz, H-1″ and H-2″).



	R^1	R^2	R^3	R^4
1	Me	H	–	–
2	Me	Gl	–	–
3	Me	Ap-Gl	H	H
4	Me	Ap-Gl	Ac	H
5	Me	Ap-Gl	Ac	Ac
6	H	Ap-Gl	H	H



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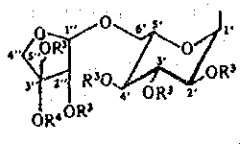

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*Part 15 in the series 'Research on African Medicinal Plants'. For Part 14 see ref. [1].

C-8), 133.23, 133.30 (C-8a and C-10a), 134.56, 134.93 (C-6 and C-7), 136.10 (C-4a), 138.57 (C-3), 162.46 (C-1), 164.74 (CO_2), 182.00 (C-10), 188.43 (C-9).

Synthesis. Nitration of 2-methylanthraquinone (5.0 g) by KNO_3 (2.5 g) in conc H_2SO_4 (25 ml) afforded 2-methyl-1-nitroanthraquinone (5.2 g) [2]. ^{1}H NMR (200 MHz, *d*-DMSO): *δ*2.37 (3H, *s*, *Me*), 7.93–7.98 (2H, *m*, *H-6 and H-7*), 8.02 (1H, *d*, *J* = 8.1 Hz, H-3), 8.11–8.23 (2H, *m*, H-5 and H-8), 8.32 (1H, *d*, *J* = 8.1 Hz, H-4). According to Scholl's method [3], 2-methyl-1-nitroanthraquinone (3.20 g) was refluxed in 30% KOH–MeOH (70 ml) to give crude 1-amino-2-carboxyanthraquinone (0.94 g), ^{1}H NMR (400 MHz, *d*-DMSO): *δ*7.21 (1H, *d*, *J* = 7.8 Hz, H-3), 7.69, 7.76 (each 1H, *t*, *J* = 7.4 Hz, H-6 and H-7), 7.95, 8.02 (each 1H, *d*, *J* = 7.4 Hz, *H-5 and H-8*), 8.18 (1H, *d*, *J* = 7.8 Hz, H-4), 9.31 (2H, *br s*, NH_2), a part of which was converted to the ethyl ester, mp 201–202° (reddish orange needles from $CHCl_3$–MeOH): ^{1}H NMR (400 MHz, $CDCl_3$): *δ*1.36 (3H, *t*, *J* = 7.1 Hz, Me), 4.33 (2H, *q*, *J* = 7.1 Hz, CH_2), 7.47 (1H, *d*, *J* = 8.1 Hz, H-3), 7.67, 7.73 (each 1H, *m*, *J* = 1.3 and 7.5, H-6 and H-7), 8.17, 8.24 (each 1H, *dd*, *J* = 1.3 and 7.5 Hz, H-5 and H-8), 8.25 (1H, *d*, *J* = 8.1 Hz, H-4) 8.56, 9.76 (*each 1H, br s, NH_2*). Reaction of 1-amino-2-carboxyanthraquinone (30 mg) with $NaNO_2$ (30 mg) in 3 M H_2SO_4 (2 ml) with ice-cooling for 1 hr was followed by addition of H_2O (4 ml) and warming at 85° for 2 hr. The crude product was refluxed for 7 hr in EtOH (0.3 ml) and $CHCl_3$ (2.5 ml) containing two drops of conc H_2SO_4. After purification by prep. TLC [Kieselgel $60F_{254}$, 1 mm, C_6H_6–Me_2CO (30:1)] 2-ethoxycarbonyl-1-hydroxyanthraquinone (8 mg) was obtained; mp 127–129° (reddish orange crystals from MeOH), which was identical to the natural product by HPLC [TSK-GEL ODS-120T, 250 × 4.6 mm, 40°, 10% aq. HOAc–MeOH (7:3→1:9)], UV and ^{1}H NMR.

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REFERENCES

1. Wijnsma, R. and Verpoorte, R. (1986) in *Progress in the Chemistry of Organic Natural Products* (Herz, W., Grisebach, H., Kirby, G. W. and Tamm, Ch., eds), Vol. 49, p. 79. Springer, Wein.
2. Wood, G. D. and Peters, A. T. (1962) *J. Chem. Soc.* 3373.
3. Scholl, R. (1913) *Monatsh. Chem.* 34, 1011.

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OCHNABIANTHRONE: A *TRANS*-9,9′-BIANTHRONE FROM *OCHNA PULCHRA**

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Key Word Index—*Ochna pulchra*; Ochnaceae; root bark; ochnabianthrone; circular dichroism.

Abstract—(−)-*trans*-2,2′-Digeranyloxy-7,7′-dimethyl-4,4′,5,5′-tetrahydroxy-9,9′-bianthrone, (−)-ochnabianthrone, was isolated from the root bark of *Ochna pulchra*. The circular dichroism curve and therefore the absolute configuration at 9,9′ (*R*,*R*′ or *S*,*S*′) is similar to that of (−)-sennidin A_1.

INTRODUCTION

Ochna pulchra Hook. f. (Ochnaceae) is a woody plant of central and southern Africa [2–4], which is commonly known in parts of Zimbabwe by the vernacular names 'umnyelenyele' or 'muparamhosva' [2, S. Sibanda and C. Nyanyira, unpublished results]. While its mature leaves are regarded as good cattle feed, the immature leaves are suspected of stock poisoning [2]. The widespread use of this plant in traditional medicine in Zimbabwe as an anti blood-parasitic agent and in the treatment of skin diseases [S. Sibanda and C. Nyanyira, unpublished results] has led to this phytochemical investigation. Previous studies on the genus resulted in the isolation of biflavonyl ethers, *C*-glycosylflavones and a furanoflavone from the aerial parts of *O. squarrosa* [5, 6], biflavones from *O. pumilia* and *O. atropurpurea* [7, 8]. In addition, glycerides had been detected in the fruits of *O. squarrosa* [9, 10] and *O. atropurpurea* [8]. However, with regards to *O. pulchra*, only glycerides had been detected in the fruit [11]. In this communication we report the isolation and character-

*Dedicated to Prof. G. B. Marini Bettolo on the occasion of his 75th birthday. Part 22 in the series 'Research on African Medicinal Plants'. For Part 21 see ref. [1].

temp. for 2 hr. After removal of the catalyst, the soln was evapd affording a residue which was crystallized from MeOH to give **2** (86 mg): mp 228–230°, IR ν_{max}^{KBr} cm^{-1}: 3220, 1723, 1703; ^1H NMR (pyridine-d_5) 5.06 (1H, *br s*, H-14α), 4.61 (1H, *dd*, 4.64 and 9.6 Hz, H-7β), 3.21 (1H, *m*, H-13α); 1.18 (3H, *d*, 8.0 Hz, Me-17), 1.07 (6H, *s*, Me-18, Me-20), 1.00 (3H, *s*, Me-19), EIMS (70 eV) *m/z*: 316 [M $-H_2O]^+$, 298 [M $-2H_2O]^+$.

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REFERENCES

1. Xu, Y. L., Sun, X. C., Sun, H. D., Lin, Z. W. and Wang, D. Z. (1981) *Acta. Bot. Yunn.* **3**, 283.
2. Liu, C. J., Zhao, Z. H., Wang, Q. D., Sun, H. D. and Lin, Z. W. (1988) *Acta. Bot. Yunn.* **10**, 471.
3. Shen, X. Y., Isogai, A., Furihata, K., Kaniwa, H., Sun, H. D. and Suzuki, A. (1989) *Phytochemistry* **28**, 855.

(21)

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DITERPENOIDS FROM *SPIROSTACHYS AFRICANA*

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Key Word Index—*Spirostachys africana*; Euphorbiaceae; heartwood; diterpenes; *ent*-hydroxybeyerenones.

Abstract—Two new beyerene derivatives; *ent*-3β,18-dihydroxy-beyer-15-ene-2-one and *ent*-3β-hydroxy-19-nor-beyer-15-ene-2,12-dione have been isolated from *Spirostachys africana* in addition to the known *ent*-3β-hydroxy-beyer-15-ene-2-one.

INTRODUCTION

Spirostachys africana Sond. is a tree of widespread occurrence in southern Africa [1, 2]. In the southeast of Zimbabwe the latex of the tree is used in traditional medicine as a purgative and as an emetic [3]. It is also known for its acrid and irritant properties [2, 4]. The crushed heartwood of the tree is an insect repellant [2] and is used to protect stored grain. Earlier phytochemical work has resulted in the isolation and characterisation of stachenone, and α-ketol, and a diosphenol. We describe the isolation and identification of two new beyerenes.

RESULTS AND DISCUSSION

Chromatography of the extract of the heartwoord of *S. africana* yielded three crystalline products. In their ^1H NMR spectra all displayed the characteristic pair of doublets arising from the *cis*-alkene moiety of the *ent*-beyer-15-ene system. The first compound was identified as the known α-ketol, *ent*-3β-hydroxy-beyer-15-ene-2-one (**1a**) [1, 5], by comparison with an authentic sample and from its ^1H NMR spectrum and that of the derived acetate **1b**. Small long range couplings ($J_{1a,3}=1.1$ Hz, $J_{1a,20}=0.8$ Hz) were observed in the spectrum of **1a** and the expected downfield shift of the H-3 signal was seen in the spectrum of the acetate **1b** (Table 1).

The second compound was shown to be the related 18-hydroxy derivative **2a**. Its ^1H NMR spectrum was similar to that of **1a** but showed the presence of only three methyl signals. Also present was a two proton doublet which was reduced to a singlet on deuterium exchange suggesting the existence of a hydroxymethyl group. Compound **2a** gave dibenzoate **2b** and significantly, a dioxane type acetal **2c** [6] on treatment with acetone and 2,2-dimethoxypropane. These observations, and the general similarity of its NMR and IR spectra of **2a** to those of **1a**, suggested the presence of a 1,3-diol system with the new hydroxy group at C-18 or C-19. As the ^1H NMR signal of the remaining methyl group of C-4 is at a relatively high field (δ0.60), more characteristic of an axial methyl group, the hydroxy group is probably on the equatorial C-18

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Estimation of the degree of ionization and the proportion of excited atoms in flame atomic spectrometry: a steady state approach

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Summary. A model is presented for the ionization of elements during flame atomic spectrometry, based on successive excitation of the electron to higher energy levels and finally the ionized state. The model is discussed in terms of a steady state involving thermal excitation, ionization, collisional excitation and collisional charge transfer interactions within the flame. Expressions are derived for the fraction ionized, and the fraction excited in terms of the rate constants for thermal excitation and radiative relaxation of the excited state. Data are presented showing good agreement between calculated and literature values for the fraction ionized for representative Group I and Group II elements.

Introduction

According to the partial local thermal equilibrium (p-LTE) theory, excitation and ionization in atomic spectrometry are unrelated phenomena occurring in parallel. Excitation is governed by the Boltzmann distribution law for bound states, while ionization is governed by Saha's equation [1], derived on the basic principle that thermal ionization may be treated as a special case of thermal dissociation.

The p-LTE theory recognises that, because of the small mass of the electron, electrons in the continuum and bound electrons in the upper atomic or excited levels near the ionization limit are in thermal equilibrium [2]. If this is indeed the case, then the ionized state should conform to the Boltzmann distribution law. According to this law, the greater the energy difference, ΔE, between the ground state and upper energy level involved in the electronic transition, the smaller will be the population of the upper state. The population of the ionic state is always greater than the population of the lowest allowed excited state by 3 to 4 orders of magnitude inspite of the fact that ΔE for ionization is much greater than ΔE for excitation to the first allowd excited state. For example, sodium has been found to be 97% ionized in a copper arc with a temperature of 5100 K, whereas the fration excited at this temperature is only 8.2×10^{-2} [3].

In a recent paper [4] we proposed a steady state kinetic model, which takes into account collisional excitation and collisional charge transfer to account for the interference effects observed when potassium is determined by flame atomic spectrometry in the presence of excess sodium as an interferent. Although the model proposed adequately explained the observed emission and absorption signal enhancement [5], in its present form the model cannot explain the apparent over-population of the ionized state as discussed above. This communication presents a modified version of our earlier model, which is designed to enable description of thermal ionization during flame atomatic spectroscopy in terms of the Boltzmann law and steady state kinetics.

Theoretical

Thermal energy in a flame is not quantified and is continuously absorbed by the atom and converted to its kinetic energy. Only when the total energy absorbed is equivalent to ΔE ($=h\nu$), the energy difference between the ground state and the first allowed excited state, will the energy be transferred to the electron to result in its transition to that excited state. The atom will continue to absorb thermal energy from the flame and the electron will be excited to the second allowed excited state, unless the time required for the atom to absorb sufficient energy for this to happen is longer than the radiative lifetime of the first excited state.

For atomic transitions the radiative lifetime, τ^*, of the excited state is given by [6]:

$$\tau^* = \frac{1.5}{(V_{max})^2 f}, \quad (1)$$

where f is the oscillator strength and V_{max} is the wave number for the wavelength of maximum emission intensity. Let the rate at which thermal energy is generated in the flame be $\epsilon = eVs^{-1}$, then

$$\epsilon t = \Delta E,$$

where t = time required by the atom to adsorb thermal energy equivalent to ΔE. Substituting for ΔE in the Boltzmann equation we have

$$n_u = n_o(g_u/g_o)\exp(-\epsilon t/kT), \quad (2)$$

where n_u and n_o are the population densities of the excited and ground state, respectively, and g_u and g_o are the statistical weights of the excited and ground state, respectively.

A NEW MODEL OF GAS LIQUID CHROMATOGRAPHY APPLYING THE KINETICS OF GASEOUS ADSORPTION AT SURFACES.

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ABSTRACT: The dependence of the adjusted retention volume, V_R^1, in gas liquid chromatograph on carrier gas flow rate, u, was studied for several solutes using 5% squalane stationary phase and 40-60 mesh fluoropak 8 as support. In all cases V_R^1 increases in a stepwise fashion as u increases. In each step the rate of increase of V_R^1 is intitially high, but gradually decreases until V_R^1 levels off. V_R^1 is further shown to be directly proportional to n, the number of adsorbant sites in the stationary phase recognised by a single analyte molecule during its passage through the column and, based on this relationship between V_R^1 and n, a new model of gas chromatography applying the kinetics of gaseous adsorption at surfaces, and whose predictions are consistent with the experimental data above, is presented.

Key words gas liquid chromatography, retention volume, carrier gas flow rate, gas adsorption kinetics

In gas liquid chromatography (GLC) the volume of carrier gas required to elute a given solute is a measure of the work required to elute the substance. This volume of carrier gas, V_R^1, is given by

$$V_R^1 = t_R^1 \; u \qquad (1)$$

Where t_R^1 is the adjusted retention time for the specific solute and u is the avarage flow rate of the carrier gas through the column. V_R^1 is a measure of the interaction energy between solute molecules and adsorbant sites on the column. It is well known in chromatography that t_R^1 is independent of sample size provided the column is not overloaded. This suggests that it is not the total interaction energy for all solute molecules adsorbed, but the avarage interaction energy experienced by each molecule as it traverses the column that datermines V_R^1. V_R^1 can therefore be assumed to depend on the nature and magnitude of the interaction energy and the density of adsorbant sites on the column. In this paper we discuss the relationship between V_R^1 and the number density, n, of adsorbant sites on the column.

THEORETICAL:

In GLC the specific volume, Vg, is given by $Vg = \frac{Vn.273}{Ws.\ Tc}$ (2)

Where Ws is the mass of liquid stationary phase in the column, Tc is the absolute column temperature and V_n is the nett retention volume. The nett retention volume takes into consideration the compressibility of the carrier gas and is given by

$$Vn = t_R^1 \bar{F} = jF_c t_R^1 \qquad (3)$$

Where $\bar{F}$ is the average flow rate corrected for compressibility, F_c is the measured flow rate corrected for temperature and for the partial pressure of water vapour, and j is the compressibility factor.

$$\text{Let } V_n.\frac{273}{T_c} = V_n^\circ = jF_c^\circ t_R^1$$

(24)

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Degradation of Glyphosate in the Aquatic Environment: An Enzymatic Kinetic Model That Takes into Account Microbial Degradation of both Free and Colloidal (or Sediment) Particle Adsorbed Glyphosate

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The kinetics of the degradation of the herbicide glyphosate in distilled water and river water containing river sediment were investigated over a period of 72 days. No appreciable degradation of glyphosate was observed in distilled water, while rapid degradation occurred in the river water plus sediment from the outset, suggesting that the degradation is mainly microbial. An immediate 35% loss from solution of glyphosate due to adsorption to suspended sediment particles and deposition to the bottom sediment was observed in the river water plus sediment experiment. Subsequently, two linear rates of degradation were observed in the water phase of this experiment: an initial rapid degradation followed by a slower breakdown. An enzymatic kinetic model is presented showing that the rate of degradation of glyphosate (G) is given by $-d(\Delta G)/dt = k_2[G_B] + k_6[GC_B]$, where k_6 and k_2 are the rate constants for sediment or colloidal particle absorbed glyphosate (GC) and the unadsorbed glyphosate (G), respectively, and the subscript B denotes microflora-bound.

INTRODUCTION

Glyphosate [*N*-(phosphonomethyl)glycine, CAS Registry No. 1071-83-6] is a postemergence nonselective broad spectrum herbicide extensively used in agriculture for the control of many annual and perennial weeds. Glyphosate is essentially nontoxic to mammals and birds, but fish and invertebrates are more sensitive to the herbicide [Weed Science Society of America (WSSA), 1983]. Recommended field application rates range from 0.34 to 4.48 kg of active ingredient/ha (WSSA, 1983). Rates of 1.8–2.2 kg/ha are recommended for the control of aquatic weeds (British Crop Protection Council, 1978).

The rate of glyphosate degradation in soil samples or soil suspended in distilled water has been found to correlate with the respiration of the sample (Ruepped et al., 1977; Sprankle et al., 1975a,b; Torstensson and Aamizepp, 1977). Since respiration is a measure of the microbial activity of the sample, the degradation of glyphosate in the soil and water environment is thought to be mainly microbial.

The degradation of glyphosate in the soil environment has been studied by Nomura and Hilton (1977) and by Hance (1976). These studies showed that the degradation of glyphosate in the soil environment involves an initial rapid degradation followed by a prolonged and slower breakdown. Nomura and Hilton (1977) suggested that this may arise from the early rapid metabolism of free glyphosate by microorganisms, followed by a slower metabolism of glyphosate adsorbed onto soil particles.

Carlisle and Trevors (1978) reviewed the use, mode of action, and degradation of the herbicide and concluded that the half-life of glyphosate in the soil environment varied considerably, ranging from less than a week to years, and appears to depend in part on the extent of soil binding and level of microbial activity. pH was found to have little effect on soil binding (Sprankle et al., 1975a,b; Hance, 1976) or rate of degradation (Moshier and Penner, 1978).

The aim of the present work was to carry out laboratory studies to elucidate further the kinetics of the degradation of the herbicide. Experimental conditions were selected to simulate as closely as possible those to be found in the natural aquatic environment. Thus, the laboratory experiments were conducted using river water and river sediment contained in plastic drums covered with clear perforated plastic and exposed to sunlight.

EXPERIMENTAL PROCEDURES

Equipment. The following were used: a high-performance liquid chromatograph, Shimadzu LC-4A system, was equipped with a 10-cm cell, a variable UV detector, and chart recorder; separations were made using a C_{18} column (0.8 × 10 cm); white plastic tanks, 150-L capacity, were used for the degradation experiments.

Materials. The following were used: Round-up (Monsanto Agricultural Products) containing 395 g of glyphosate/L, supplied by the Zimbabwe Fertilizer Co.; ethyl acetate, sodium dihydrogen phosphate buffer, tetraethylammonium bromide (AR grade), acetonitrile (HPLC grade); distilled water; river water and sediment collected from the Mukuvisi River, Harare, Zimbabwe (the river had never been treated with glyphosate); 2,4-dinitrochlorobenzene (reagent grade); sodium bicarbonate and sodium hydroxide (AR grade). The glyphosate standard was obtained by precipitation from Round-up and recrystallization from ethanol, melting point 199 °C (literature 200 °C).

Procedure. One lot each of 100 L of river water and distilled water was charged into separate 150-L plastic tanks, and the levels were marked. To the tank containing river water was added 1.93 kg of the sediment from the Mukuvisi River. Thirty-eight milliliters of Round-up was then added to each tank (to give a solution containing approximately 150 ppm of glyphosate), and then contents were thoroughly mixed. Samples for analysis at zero time were taken immediately after the mixing. The new levels of water in the tanks were marked. The tanks were then covered with transparent perforated polythene and left exposed to the sun on the roof of the University of Zimbabwe Chemistry Department building. Thereafter, samples were taken periodically over a period of 72 days, each time compensating for evaporation prior to sampling and marking the new level of water after each sampling. Sediment samples were scooped from the bottom of the tank before any agitation of the tank.

Once collected, the samples were frozen in plastic bottles until required for analysis, whereupon they were thawed and mixed thoroughly before extraction and derivatization of the glyphosate for HPLC analysis.

Extraction, Derivatization, and HPLC Analysis. Water samples were filtered through Whatman No. 1 filter paper,

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(25)

Organochlorine pesticide residues in the sediments of selected river bays in Lake Kariba, Zimbabwe

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ABSTRACT

Sediment samples from seven of the major river bays on the Zimbabwe side of Lake Kariba were analysed for organochlorine pesticide residues by capillary gas chromatography and electron capture detection. The results obtained confirm contamination of most of the bays by DDT and its metabolites, endosulphan, aldrin, dieldrin, endrin and heptachlor.

Key words: Author please supply 5 keywords

INTRODUCTION

Environmental pollution has become a global concern to which developing countries are slowly awakening, too. Of major concern in Zimbabwe is the impact of the increasing use of organochlorine pesticides to control agricultural pests, including tsetse fly (*Glossina* ssp.) and malaria vectors.

Pesticide sprays for tsetse fly control in Zimbabwe began in the early 1960s. Pesticides which have been used include dieldrin (1962–1967) and DDT (1968 to the present) (Whitwell et al., 1974; Mpofu, 1987). Endosulphan and deltamethrin are also used, especially in aerial sprays (Chapman, 1976). In addition to its use in the control of tsetse fly and malaria vectors, DDT was used extensively in agriculture prior to 1983 when the use of DDT

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Author: Please supply original figures.

IMPORTANT

2.6.93

(26)

Photolysis of Triclocarban in Dilute Aqueous and Aqueous Ethanol Solution

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Appendix-13 Environmental Law in Zimbabwe {Water (Effuluent and Waste Water Standards) Regulations 1977}

Statutory Instrument 434 of 1982.

[ACT 41/76

Water (Effluent and Waste Water Standards) (Amendment) Regulations, 1982 (No. 1)

IT is hereby notified that the Minister of Water Resources and Development has, in terms of section 135 of the Water Act, 1976, made the following regulations: —

1. These regulations may be cited as the Water (Effluent and Waste Water Standards) (Amendment) Regulations, 1982 (No. 1).

2. The Second Schedule to the Water (Effluent and Waste Water Standards) Regulations, 1977, published in Rhodesia Government Notice 687 of 1977, is amended in item 11 by the deletion, from the Table, of—

"Ammonia free and saline (as N)	0,5	0,5"

and the substitution of—

"Ammonia free (as N)	0,2	0,2".

Supplement to the Zimbabwean Government Gazette dated the 2nd July, 1982. Printed by the Government Printer, Harare.

11. The maximum permissible concentrations of chemical constituents permissible in the water which is discharged or disposed of in a Zone I or Zone II catchment area shall be as specified in the following table:

TABLE

MAXIMUM PERMISSIBLE CONCENTRATIONS OF CERTAIN CHEMICAL CONSTITUENTS

Constituent	Maximum concentration in milligrams per litre	
	Zone I catchment area	Zone II catchment area
Ammonia free and saline (as N)	0,5	0,5
Arsenic (as As)	0,05	0,05
Barium (as Ba)	0,1	0,5
Boron (as B)	0,5	0,5
Cadmium (as Cd)	0,01	0,01
Chlorides (as Cl)	50	100
Chlorine residual (as free chlorine)	Nil	0,1
Chromium (as Cr)	0,05	0,05
Copper (as Cu)	0,02	0,5
Cyanides and related compounds (as CN)	0,2	0,2
Detergents (as manoxol -OT)	0,2	1,0
Fluoride (as F)	1,0	1,0
Iron (as Fe)	0,3	0,3
Lead (as Pb)	0,05	0,05
Manganese (as Mn)	0,1	0,1
Mercury (as Hg)	0,5	0,5
Nickel (as Ni)	0,3	0,3
Nitrogen total (as N)	10,0	10,0
Phenolic compounds (as phenol)	0,01	0,1
Phosphates total (as P)	1,0	1,0
Sulphate (as SO_4)	50	200
Sulphides (as S)	0,05	0,2
Zinc (as Zn)	0,3	1,0
Total heavy metals	1,0	2,0

12. The water shall not contain any detectable quantities of pesticide, herbicide or insecticide, nor shall it contain any other substances not referred to elsewhere in these standards, in concentrations which are poisonous or injurious to human, animal, vegetable or aquatic life.

SECOND SCHEDULE (*Section 3*)

PRESCRIBED STANDARDS OF EFFLUENT OR WASTE WATER

1. The water shall not contain any colour or have any odour or taste capable of causing pollution.

2. The water shall not contain any radioactive substances capable of causing pollution.

3. The pH of the water shall be, where discharged or disposed of—
   (a) in a Zone I catchment area, between 6,0 and 7,5;
   (b) in a Zone II catchment area, between 6,0 and 9,0.

4. The temperature of the water at the point of discharge shall not exceed—
   (a) in a Zone I catchment area, 25 °C;
   (b) in a Zone II catchment area, 35 °C.

5. The water shall contain dissolved oxygen to the extent of at least, where discharged or disposed of—
   (a) in a Zone I catchment area, 75 *per centum* saturation;
   (b) in a Zone II catchment area, 60 *per centum* saturation.

6. The chemical oxygen demand of the water, after applying chloride correction, shall not exceed, where discharged or disposed of—
   (a) in a Zone I catchment area, 30 milligrams per litre;
   (b) in a Zone II catchment area, 60 milligrams per litre.

7. The oxygen absorbed by the water shall not exceed, where discharged or disposed of—
   (a) in a Zone I catchment area, 5 milligrams per litre;
   (b) in a Zone II catchment area, 10 milligrams per litre.

8. The total undissolved solids content of the water at the point of discharge shall not be greater than—
   (a) in a Zone I catchment area, 10 milligrams per litre;
   (b) in a Zone II catchment area, 25 milligrams per litre.

9. The total dissolved solids content of the water at the point of discharge shall not—
   (a) in a Zone I catchment area, increase the total dissolved solids content of the receiving water by more than 100 *per centum* and the total dissolved solids content of the effluent shall not exceed 100 milligrams per litre;
   (b) in a Zone II catchment area, exceed 500 milligrams per litre.

10. The water shall not contain soap, oil or grease in quantities greater than, where discharged or disposed of—
   (a) in a Zone I catchment area, nil;
   (b) in a Zone II catchment area, 2,5 milligrams per litre.

FIRST SCHEDULE *(Section 2)*

ZONES I AND II CATCHMENT AREAS

1. *Zone I catchment areas*	*Locality*
The river catchment area of—	
(a) the Gairezi River and its tributaries	Inyanga district
(b) the Pungwe River and its tributaries	Inyanga district
(c) the Hondi River and its tributaries	Inyanga district
(d) the Nyamkwarara River and its tributaries	Inyanga district
(e) the Inyangombe River and its tributaries to its confluence with the Nyajezi River	Inyanga and Makoni districts
(f) the Nyajezi River and its tributaries to its confluence with the Inyangombe River	Inyanga district
(g) the Odzi River and its tributaries to its confluence with the Odzani River	Inyanga district
(h) the Odzani River and its tributaries to its confluence with the Odzi River	Inyanga district
(i) the Mazonwe River and its tributaries	Umtali district
(j) the Umvumvumvu River and its tributaries to its confluence with the Nyambewa River	Melsetter district
(k) the Nyambewa River and its tributaries to its confluence with the Umvumvumvu River	Melsetter district
(l) the Nyanyadzi River and its tributaries to its confluence with the Biriwiri River	Melsetter district
(m) the Biriwiri River and its tributaries to its confluence with the Nyanyadzi River	Melsetter district
(n) the Lusitu River and its tributaries	Melsetter district
(o) the Busi River and its tributaries	Chipinga district

2. *Zone II catchment areas* ← HARARE CITY

All river catchment areas other than those specified under Zone I.

of the effluent or waste water shall be taken, at the point of discharge, at approximately equal intervals of time over a minimum period of approximately four hours within any twenty-four-hour period;

(b) temperature, pH and dissolved oxygen readings shall be taken on individual samples at the time of sampling, and all samples shall comply with the standards specified in respect of temperature, pH and dissolved oxygen in the First Schedule;

(c) where full laboratory facilities do not exist on the site for the determination of dissolved oxygen, the oxygen in the sample may be fixed at the time of sampling by adding the sulphuric acid, the permanganate, the oxalate, the manganous sulphate and the alkaline iodide only:

Provided that—

(i) the stopper of the sample container shall be replaced and the solution shall be well mixed;

(ii) the remaining steps shall be carried out later in the laboratory.

Repeals

5. The Water Pollution Control (Waste and Effluent Water Standards) Regulations, 1971, published in Rhodesia Government Notice No. 609 of 1971, are repealed.

Rhodesia Government Notice No. 687 of 1977.

[ACT 41/76

Water (Effluent and Waste Water Standards) Regulations, 1977

IT is hereby notified that the Minister of Water Development has, in terms of section 135 of the Water Act, 1976, made the following regulations: —

Title

1. These regulations may be cited as the Water (Effluent and Waste Water Standards) Regulations, 1977.

Interpretation

2. In these regulations—

"heavy metal" means a metal having a specific gravity greater than 5,0;

"Zone I catchment area" means a Zone I catchment area specified in the First Schedule;

"Zone II catchment area" means a Zone II catchment area specified in the First Schedule.

Prescribed standards of quality for effluent and waste water

3. The standards of quality, prescribed for the purposes of paragraph (a) of subsection (2) of section 101 of the Act, to which effluent or waste water which has been produced by, or results from, the use of water for any purpose, and which is discharged or disposed of into a public stream, private water, public water or underground water, whether directly or through drainage or seepage, shall conform, shall be as set out in the Second Schedule.

Sampling procedure

4. The following requirements shall be complied with in respect of any sample which may be taken or required to be taken of effluent or waste water for the purposes of Part IX of the Act—

(a) a composite sample for the purpose of analysis for all tests, other than those for temperature, pH and dissolved oxygen, shall be taken by combining individual samples so that a minimum of five samples of equal volume of not less than five hundred millilitres each

Appendix-14 Arrangement of Equipment in Building of The Chemistry Department

1) Arrangement List of Planning Equipment in Building of The Chemistry Department

2) Arrangement Design of Planning Equipment in Building of The Chemistry Department

(1) Ground Floor Plan

(2) First Floor Plan

(3) Second Floor Plan

Appendix-14 Arrangement of Equipment in Building of The Chemistry Department

No.	Equipment	Existing Building	New Building
01	Fourier Transform Nuclear Magnetic Resonance Spectrometer	C022(COM)	
02	Gas Chromatograph Mass Spectrometer	C024(COM)	
03	Fourier Transform Infrared Spectrophotometer	C023(COM)	
04	Ultra violet/Visible Spectrophotometer	C025(COM)	C119(AC)
05	Gas Chromatograph	C025(COM) 39(1F,OC)	C117(AC)
06	High Performance Liquid Chromatograph	C026(COM)	C122(AC)
07	Fluorophotometric Analyzer	54(2F,OC)	
08	Atomic Absorption Spectrophotometer	73,76,78 (1F,IC)	
09	Personal Computer		C015(COM)
10	Polarograph	73(1F,IC)	
11	Thermal Analyzer	76(1F,IC)	

No.	Equipment	Existing Building	New Building
12	Liquid Nitrogen Plant	21(COM)	
13	Droplet Counter Current Chromatograph	39(1F, OC)	
14	Fourier Transform Infrared Spectrophotometer		C119(AC)
15	Ion Chromatograph		C112(AC)
16	Polarimeter	42(1F, OC/DR)	
17	Coulometer		C120(AC)
18	pH Meter/Ion Meter	OCL-2(2F, OC)	C116(AC)
19	X-Y Recorder	58(2F, COM)	
20	Recorder		C220(COM)
21	Photo Copy	48(1F, COM)	
22	Muffle Furnace	64(1F, AC&IC)	C116(COM)
23	Freeze Dryer	C029(COM)	
24	Heavy Duty Juice Extractor	OCL-2(2F, OC)	
25	Surface Area Apparatus	73(1F, IC)	

No.	Equipment	Existing Building	New Building
26	Peristaltic Pump		C116(AC) C219(PC)
27	Lotation Locurar Counter Current Chromatograph	37(1F,0C)	
28	Table Top Centrifuge	OCL-2(2F,0C)	
29	Analytical Balance	FYL(COM)	C118(AC) C121(AC) C218(PC)
30	Rotary Evaporator	OCL-G(0C) OCL-2(0C)	C116(AC)
31	Glassblowing Equipment		C017(COM)
32	Bomb Calorimeter		C219(PC)
33	Micro Stopped Flow Spectrophotometer		C219(PC)
34	NOx Analyzer	OCL-2(0C)	
35	Circular Dichroism Optical Rotary Dispersion	OCL-2(0C)	
36	Conductivity Meter		C212(PC)
37	Heating Mantle	OCL-G(0C)	

No.	Equipment	Existing Building	New Building
38	Vaccum Pump	OCL-G(OC)	C116(AC) C219(PC)
39	High Pressure Autoclave	72(1F, IC)	
40	Electric Top Loading Balance	OCL-G(OC) FYL(COM)	C116(AC) C216(PC)
41	Education Video Material	7(COM)	
42	Volt Meter		C216(PC)
43	Viscometer		C217(PC)
44	Abbe Refractometer		C216(PC)
45	Melting Point Apparatus	OCL-G(OC) FYL(COM)	
46	Polarising Microscope		C217(PC)
47	Ice Maker	FYL(COM)	
48	Over Head Projector	7(COM)	
49	Slide Projector	7(COM)	
50	Wayne Kerr Bridge		C212(PC)
51	Multimeter		C216(PC)

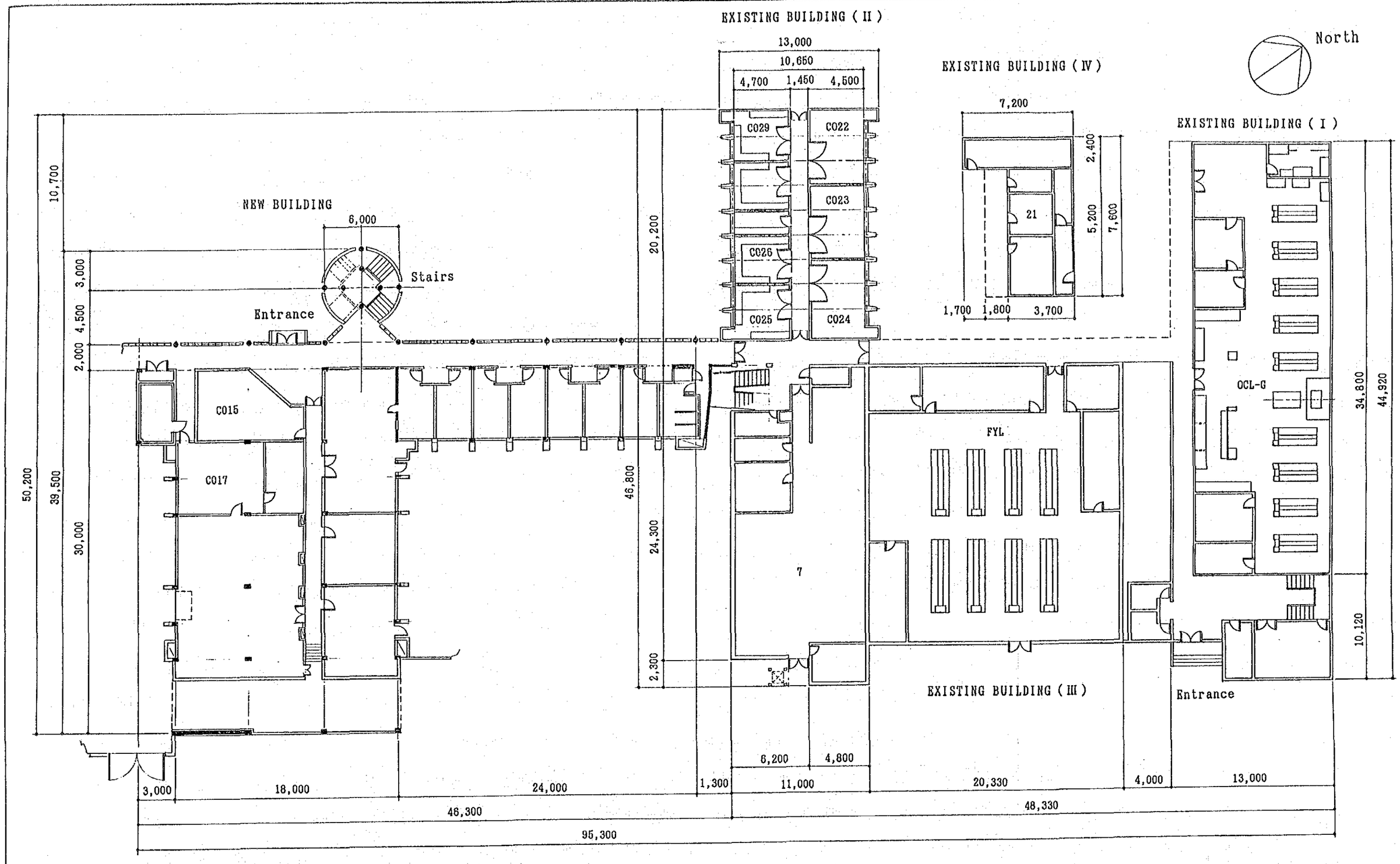
No.	Equipment	Existing Building	New Building
52	Soxhlet Extractor	OCL-G(OC)	
53	Hot Plate & Magnetic Stirrer	OCL-G(OC)	C116(AC)
54	Wheaton Micro Sublimation Apparatus	OCL-G(OC)	
55	Magnetic Balance (Gouy Type)		C218(PC)

AC: Analytical Chemistry
IC: Inorganic Chemistry
OC: Organic Chemistry
PC: Physical Chemistry
COM: Common
OCL: Laboratories of Organic Chemistry
FYL: First Year's Laboratories
DR: Dark Room
GF: Ground Floor
1F: Second Floor
2F: Third Floor

GROUND FLOOR

ROOM NO.	CODE NO.	DESCRIPTION	Q'TY
NEW BUILDING			
C015	09	Personal Computor	12
C017	31	Glass Blowing Equipment and Annealing Oven	1
EXISTING BUILDING (I)			
OCL-G	30-1	Rotary Evaporator	2
"	37-1	Heating Mantle	4
"	37-2	Heating Mantle	4
"	37-3	Heating Mantle	4
"	37-4	Heating Mantle	4
"	38-1	Vacuum Pump	1
"	38-2	Vacuum Pump	3
"	40-2	Electric Top Loading Balance	2
"	40-3	Electric Top Loading Balance	3
"	45	Melting Point Apparatus	2
"	52-1	Soxhlet Extractor	3
"	52-2	Soxhlet Extractor	3
"	53	Hot Plate with Magnetic Stirrer	6
"	54	Wheaton Micro Sublimation Apparatus	1
EXISTING BUILDING (II)			
C022	01	FT-NMR (Fourier Transform Nuclear Magnetic Resonance Spectrometer)	1
C023	03	FT-IR (Fourier Transform Infrared Spectrophotometer)	1
C024	02	GC-MS (Gaschromatograph Mass Spectrometer)	1
C025	04-1	UV/VIS (Ultraviolet and Visible Spectrophotometer)	1
"	05-1	GC (Gaschromatograph)	2
C026	06-1	HPLC (High Performance Liquid Chromatograph)	1
C029	23	Freeze Dryer	1
7	41	Education Video Material	1
"	48	Overhead Projector	4
"	49	Slide Projector	2

ROOM NO.	CODE NO.	DESCRIPTION	Q'TY
EXISTING BUILDING (Ⅲ)			
FYL	29-2	Analytical Balance	6
"	40-1	Electric Top Loading Balance	5
"	45	Melting Point Apparatus	1
"	47	Ice Maker	1
EXISTING BUILDING (Ⅳ)			
21	12	Liquid Nitrogen Plant	1



THE UNIVERSITY OF ZIMBABWE, THE CHEMISTRY DEPARTMENT

Ground Floor Plan

Scale : 1/200, Unit : mm

1 st. FLOOR

ROOM NO.	CODE NO.	DESCRIPTION	Q'TY
NEW BUILDING			
C112	15	Ion Chromatograph	1
C116	18	pH Meter/Ion Meter	6
"	22-1	Muffle Furnace	1
"	22-2	Muffle Furnace	3
"	26	Peristaltic Pump	2
"	30-1	Rotary Evaporator	2
"	38-1	Vacuum Pump	2
"	40-1	Electric Top Loading Balance	2
"	40-2	Electric Top Loading Balance	2
"	53	Hot Plate with Magnetic Stirrer	4
C117	05-2	GC (Gaschromatograph)	2
C118	29-2	Analytical Balance	6
C119	04-2	UV/VIS (Ultraviolet / Visible Spectrophotometer)	1
"	14	FT-IR (Fourier Transform Infrared Spectrophotometer)	1
"	17	Coulometer	1
C121	29-2	Analytical Balance	6
C122	06-2	HPLC (High Performance Liquid Chromatograph)	1
EXISTING BUILDING (I)			
37	27	Rotation Locular Counter Current Chromatograph	1
39	05-2	GC (Gaschromatograph)	1
"	13	Droplet Counter Current Chromatograph and Fraction Collector	1
42	16	Polarimeter	1
48	21	Photo Copy	1
EXISTING BUILDING (II)			
64	22-3	Muffle Furnace	1
"	22-4	Muffle Furnace	1
72	39	High Pressure Autoclave	1

ROOM NO.	CODE NO.	DESCRIPTION	Q'TY
EXISTING BUILDING (II)			
73	08-2	Atomic Absorption Spectrophotometer	1
"	10	Polarograph	1
"	25	Surface Area Apparatus	1
76	11	TG/DTA (Combined Thermal Analyzer)	1
78	08-1	Atomic Absorption Spectrophotometer	1

EXISTING BUILDING (II)

North

EXISTING BUILDING (I)

NEW BUILDING

Stairs

C112

C116

C122 C121 C120 C119 C118 C117

64

72

76

73

78

39

42

37

48

10,700

50,200

39,500

30,000

3,000

4,500

2,000

6,000

10,650

20,200

44,500

24,300

34,800

44,920

10,120

3,000 18,000 24,000 1,300 11,000 24,330 13,000

46,300 48,330

95,300

THE UNIVERSITY OF ZIMBABWE, THE CHEMISTRY DEPARTMENT

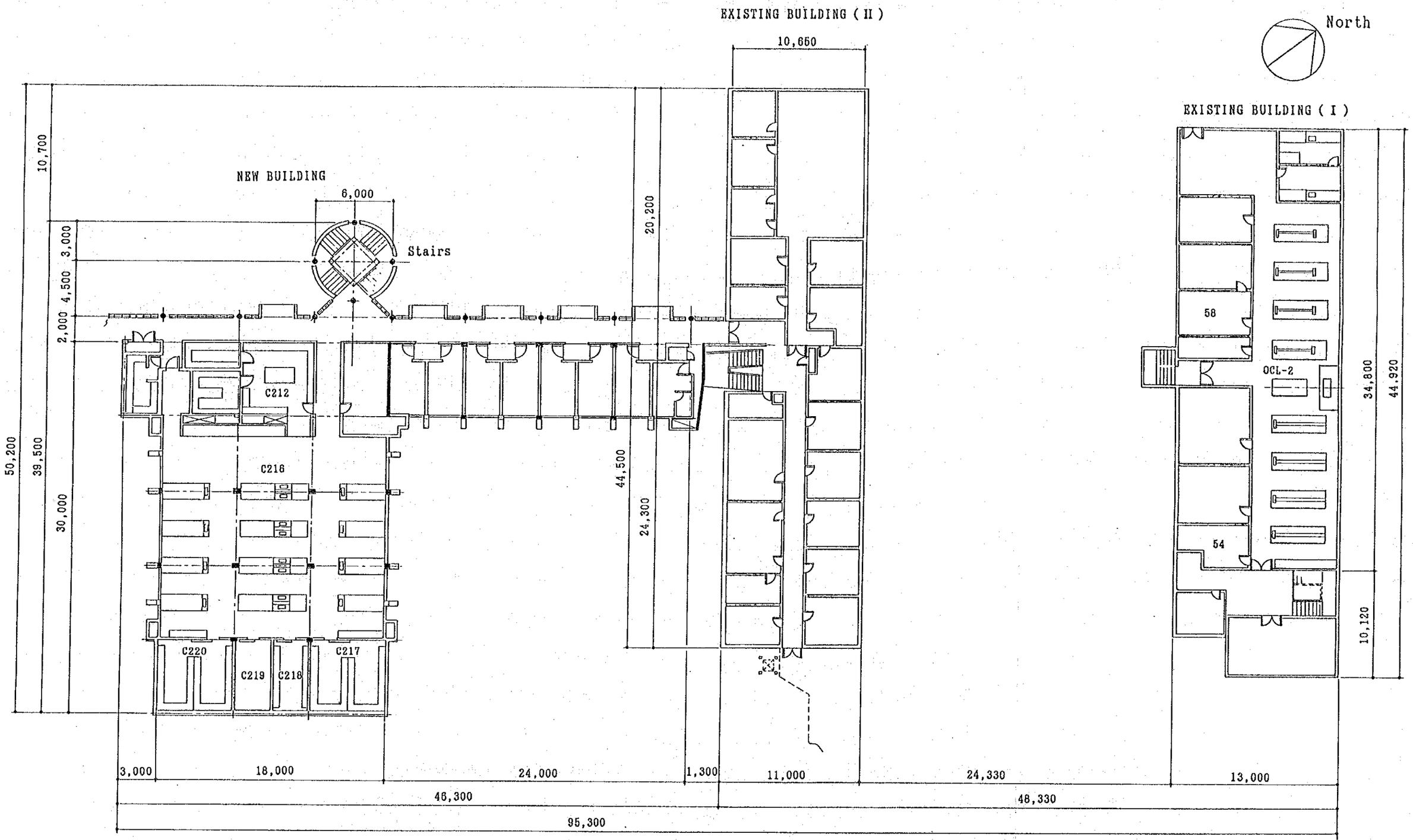
1st. Floor Plan

Scale : 1/200, Unit : mm

2 nd FLOOR

ROOM NO.	CODE NO.	DESCRIPTION	Q'TY
NEW BUILDING			
C212	36	Conductivity Meter	5
"	50	Wayne Kerr Bridge	1
C216	40-2	Electric Top Loading Balance	2
"	40-3	Electric Top Loading Balance	3
"	42	Digital Volt Meter	12
"	44	Abbe refractometer	1
"	51	Multimeter	2
C217	43-1	Viscometer (Brockfield Type)	1
"	43-2	Viscometer (Saybolt Type)	1
"	46	Polarising Microscope	1
C218	29-1	Analytical Balance	6
"	55	Gouy's Magnetic Balance	1
C219	26	Peristaltic Pump	2
"	32	Bomb Calorimeter	1
"	33	Stop Flow System	1
"	38-3	Vacuum Pump	4
C220	20	Recorder	1
EXISTING BUILDING (I)			
54	07	Fluorophotometric Analyzer	1
58	19	X-Y Recorder	1
OCL-2	18	pH Meter/Ion Meter	6
"	24	Heavy Duty Juice Extractor	1
"	28	Table Top Centrifuge	1

ROOM NO.	CODE NO.	DESCRIPTION	Q'TY
EXISTING BUILDING (I)			
OCL-2	30-1	Rotary Evaporator	2
"	30-2	Rotary Evaporator	1
"	30-3	Rotary Evaporator	1
"	34	NOx Analyzer	1
"	35	CD-ORD (Circular Dichroism/Optical Rotatory Dispersion)	1



THE UNIVERSITY OF ZIMBABWE, THE CHEMISTRY DEPARTMENT

2nd Floor Plan

Scale : 1/200, Unit : mm

Appendix-15 List of Collected Information in Zimbabwe

— The Basic Design Study Team —

1. SECOND FIVE-YEAR NATIONAL DEVELOPMENT PLAN 1991-1995
2. SECOND FIVE-YEAR NATIONAL DEVELOPMENT PLAN 1986-1990
3. ATOMOSPHERIC POLLUTION PREVENTION PUBLIC HEALTH
4. HARARE (WASTE-MANAGEMENT) BY-LAWS 1979
5. Organisation Structure of The Zimbabwe Government

6. Minister of Higher Education - Vote 16
7. Minister of Higher Education - Organisation Chart
8. Annual Report of the Secretary for Higer Education, for the year ended 31st. December, 1990
9. Annual Report of the Secretary for Higer Education, for the year ended 31st. December, 1989
10. Principal Officers of The Unversity

11. University of Zimbabwe, Faculty of Science
12. University of Zimbabwe, 1992, Calendar
13. University of Zimbabwe, The Vice-chancellor's Annual, 1991
14. University of Zimbabwe, Technical Staff Structure Chemistry Department
15. University of Zimbabwe, Staff Abilities and Their Research Forcus

16. University of Zimbabwe, Chemistry Department
17. University of Zimbabwe, Total Number of Students by Dept., Faculty of Science, 1991-1993
18. University of Zimbabwe, Chemistry Department Student Numbers, 1993
19. University of Zimbabwe, Chemistry Department Student Numbers, 1980-1993
20. University of Zimbabwe, Chemistry Department Number of Students by cource

21. University of Zimbabwe, Budget of Dept. of Chemistry for Teaching
22. University of Zimbabwe, Chemistry Timetable, BSc. PartIII and BSc Hornours, 1993-First Semester
23. University of Zimbabwe, Quarterly Digest of Statistics
24. University of Zimbabwe, Chemistry Department Priority List
25. University of Zimbabwe, Curriculum Vitae

26. University of Zimbabwe, Instrument Maintenance/Repair Record
27. University of Zimbabwe, Operation Manual, Instructions for Metrohm pH Meter
28. University of Zimbabwe, "INTEGRATOR"
29. Standards Accociation of Zimbabwe
30. INCHEM, Membership List of Industrial Chemical Association As of 19 August, 1993