Contributions of P. C. Rây in organic synthesis

Animesh Chakravorty

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata-700 032, India

E-mail: icac@iacs.res.in

Manuscript received 26 September 2016, accepted 18 October 2016

Abstract: During most of his career Rây was busy with his work in the inorganic chemistry area. But he also had a long-standing interest in organic synthesis which finally got expressed only in terminal years of his career. We consider in this work two of his main endeavours in this area. First, synthesis of thio ketones in general and thiocamphor and some related species in particular using hydrogen sulfide under acid catalysis as the reagent. Second, his introduction of thallium fluoride as a reagent for organic fluorination. The cases of fluorocarboxylate esters, fluoroketones and some more will be cited.

Keywords: Organic synthesis, thio ketones, thiocamphor, fluorocarboxylates, fluoroketone, H$_2$S-HCl, TlF.

Cyclic voltammetric and spectral studies of some complexes in copper(II)-diethylidithiocarbamate-2-methylimidazole mixed ligand systems

Krishna Srivastava*, Alka Srivastava, Devendra K. Gautam and Jagdish Prasad

Department of Chemistry, University of Allahabad, Allahabad-211 002, Uttar Pradesh, India

E-mail: dr_krishna_s@yahoo.co.in

Manuscript received online 18 April 2016, accepted 03 May 2016

Abstract: The electrochemical and spectral properties of copper(II) complexes in Cu$^{II}$-diethylidithiocarbamate-2-methylimidazole mixed ligand systems in different molar ratios (1 : 1 : 2, 1 : 1 : 100, 1 : 2 : 2 and 1 : 2 : 100) in acetone medium containing 0.2 M sodium perchlorate as a supporting electrolyte have been studied by using cyclic voltammetry (CV). UV-Visible absorption spectra of the above Cu$^{II}$ : Et$_2$-dtc$^-$. 2-MeIm systems were also recorded in acetone. On the basis of CV results, it has been concluded that two complex species are present in equilibrium in solution in Cu$^{II}$ : Et$_2$dtc : 2-MeIm mixed-ligand systems in 1 : 1 : 2, 1 : 2 : 2 and 1 : 2 : 100 molar ratios and only one mixed-ligand complex species is present in 1 : 1 : 100 molar ratio.

Keywords: Cyclic voltammetry, diethylidithiocarbamate, 2-methylimidazole, Cu$^{II}$-mixed-ligand complexes.

Syntheses, spectral characterization and antimicrobial studies of the coordination compounds of the Schiff base containing diacetyl moiety
Dinesh Kumar*, Nidhi Sharma and Silky Chadda
Department of Chemistry, National Institute of Technology, Kurukshetra-136 119, Haryana, India
E-mail: dkumar_nitk@yahoo.com, nidhi.sunny20@gmail.com, silkychadda2010@gmail.com

Manuscript received online 12 August 2016, accepted 15 August 2016

Abstract: A new dibasic tetradentate ONNO donor Schiff base, LH₄ (1) has been synthesized by the
nucleophilic addition reaction followed by the elimination of two water molecules between diacetyl and 3-
ketobutanehydrazide (KBHz) in 1 : 2 molar ratio. The corresponding air-stable, non-electrolytic (Λ_M =
2.4–8.9 mho cm² mol⁻¹ in DMSO), six-coordinate coordination compounds, [M(LH₂)(H₂O)₂] (2) (where M
= Mn, Co, Ni, Zn, Cd) have also been synthesized by refluxing a MeOH solution of 1 and the appropriate
ions in 1 : 1 molar ratio. The latter have been characterized on the basis of elemental analyses, molecular
weight, molar conductance, spectral (IR, reflectance, ¹H NMR) studies, TGA and magnetic susceptibility
measurements. The molecular structure of the compounds have been optimized by MM2 calculations.
They exhibit antimicrobial activities against Gram-positive bacteria (S. aureus, B. subtilis) and yeast (S.
cerevisiae, C. albicans), however, they do not exhibit any activity against Gram-negative bacteria (E. coli,
P. aeruginosa).

Keywords: Coordination compounds, diacetyl, 3-ketobutanehydrazide, molecular modelling, MM2, octahedral
compounds, Schiff base, spectral studies, thermogravimetric analysis.

J. Indian Chem. Soc.,
Vol. 93, December 2016, pp. 1351-1355

Interaction of catechol with Fe³⁺ tripodal ligand complex in aqueous
surfactant medium: A kinetic approach

Pradyut Sarma*, Prabin Kr. Baruah and Okhil Kr. Medhi

Departments of Chemistry, Arya Vidyapeeth College, Guwahati-781 016, Assam, India
E-mail: gu_123456@yahoo.com

Manuscript received online 10 August 2016, accepted 19 August 2016

Abstract: The oxygenation reaction of catechol (cat²⁻) with ferric complex [Fe(NTA)] (NTA =
nitrilotriacetate) has been studied in aqueous surfactant medium. The oxygenation reaction is observed to
follow pseudo-first order pathway in cationic, anionic and non-ionic surfactant medium. These rate
constant values are validated and enzyme kinetics of the oxygenation reaction has also been thoroughly
examined. The results of the kinetics experiment may be considered as dioxygenase enzyme mimics.

Keywords: Catechol, tripodal ligand, surfactant, oxygenation reaction, enzyme kinetics.

J. Indian Chem. Soc.,
Vol. 93, December 2016, pp. 1357-1364

Kinetics and mechanism of oxidation of some heterocyclic aldehydes by
benzimidazolium fluorochromate in aqueous acetic acid medium

V. Saleem Malik, I. Vannamuthu, S. Syed Shafi and S. Sheik Mansoor*

J. Indian Chem. Soc.,
Vol. 93, December 2016, pp. 1365-1371
Abstract: The oxidation of some heterocyclic aldehydes (HA) like 2-furaldehyde, 2-pyrrole-carbaldehyde and 2-thiophene-carbaldehyde by benzimidazolium fluorochromate (BIFC) have been studied in aqueous acetic acid medium. The oxidation leads to the formation of the corresponding carboxylic acids. The reaction is first order with respect to BIFC, heterocyclic aldehydes and [H+] and the reaction is catalyzed by hydrogen ions. The reaction has been studied in different percentage of acetic acid-water mixture. A suitable mechanism has been proposed.

Keywords: Benzimidazolium fluorochromate, heterocyclic aldehydes, kinetics, oxidation.

Speciation of ternary complexes of L-histidine and L-glutamic acid with some toxic metal ions in polar medium

K. Bharath Kumar Naik, S. Raju, B. Ananda Kumar and G. Nageswara Rao*
School of Chemistry, Andhra University, Visakhapatnam-530 003, Andhra Pradesh, India
E-mail: gollapallinr@yahoo.com

Abstract: Formation of ternary complexes of PbII, CdII and HgII ions with L-histidine and L-glutamic acid was studied pH metrically in the concentration range of 0–60% v/v DMSO-water mixtures maintaining an ionic strength of 0.16 mol L–1 at 303.0 K. Alkalimetric titrations were carried out in different concentrations of metal (M = PbII, CdII and HgII) to histidine (L) to glutamic acid (X). Stability constants of ternary complexes were calculated and various models were refined with MINIQUAD75. The best fit chemical models were selected based on statistical parameters and residual analysis. The species detected are M(LH2)(XH), M(LH)(XH) and M(L)(LH)(XH), for PbII and CdII, and M(LH2)(XH) for HgII. The chemical speciation, metal bioavailability and transportation are explained based on the stability constants.

Keywords: Chemical speciation, mixed-ligand complexes, histidine, glutamic acid, toxic metals, DMSO.

Extraction studies of FeIII metal ion from hydrobromic acid medium using Cyanex-923 extractant

A. R. Bhoir and S. D. Pawar*
Department of Chemistry, University of Mumbai, Lokmanya Tilak Bhavan, Vidyanagari, Santacruz (E), Mumbai-400 098, India, E-mail: sureshpawar2004@gmail.com
Abstract: A systematic study of solvent extraction of Fe$^{III}$ from hydrobromic acid medium using neutral phosphine oxide extractant, Cyanex-923 in toluene has been proposed. This metal ion was found to be quantitatively extracted with Cyanex-923 in toluene in the acidic range of 6–7 M HBr and from the organic phase it is stripped back into the aqueous phase with water. The effect of HBr concentration, reagent concentration, equilibrium period, effect of diluents, effect of equilibration period and stripping agent on the extraction of Fe$^{III}$ has been studied. The stoichiometry of the extracted species was determined on the basis of slope analysis method. Based on these results a sequential procedure for their separation from each other was developed.

Keywords: Extraction, iron, HBr, Cyanex-923, stripping, separation.

Oxidation studies of formic and oxalic acids by morpholinium fluorochromate: Kinetic and mechanistic study

Vasudha Ranga, Umashankar Soni, Ammilal Rao, Priyanka Purohit and Pradeep K. Sharma*

Department of Chemistry, J. N. V. University, Jodhpur-342 005, Rajasthan, India

E-mail: drpkvs27@yahoo.com

Abstract: Kinetics and mechanism of oxidation of formic and oxalic acids by morpholinium fluorochromate (MFC) have been studied in dimethylsulphoxide. The main product of oxidation is carbon dioxide. The reaction is first order with respect to MFC. Michaelis-Menton type of kinetics were observed with respect to the reductants. The reaction is acid-catalysed and the acid dependence has the form: $k_{obs} = a + b[H^+]$. The oxidation of $\alpha$-deuterioformic acid exhibits a substantial primary kinetic isotope effect ($k_H/k_D = 5.30$ at 298 K). The reaction has been studied in nineteen different organic solvents and the solvent effect has been analysed using Taft's and Swain's multiparametric equations. The temperature dependence of the kinetic isotope effect indicates the presence of a symmetrical cyclic transition state in the rate-determining step. Suitable mechanisms have been proposed.

Keywords: Kinetics, mechanism, fluorochromate, organic acids, oxidation.

Preliminary clinical investigation on fluoride contamination in Nalhati subdivision (West Bengal); possible structural changes of water due to fluoride ion and related clinical aspects

A. S. Datta$^a$, R. Singh$^b$, D. Basu$^c$ and S. C. Lahiri$^a$

$^a$Central Forensic Science Laboratory, 30, Gorachand Road, Kolkata-700 014, India

E-mail: sujitclahiri@yahoo.com  Fax: 033-22849442

$^b$Department of Biochemistry, SSKM Hospital, Kolkata, India

$^c$Department of Biochemistry, Malda Medical College, Malda, West Bengal, India
Abstract: Fluorosis is widely prevalent in Nalhati in Bhubneshwar District. Attempts were made for a preliminary study on the clinical aspects of fluorosis in fluoride affected victims in Nalhati. Though the tap water is relatively free from fluoride contamination but fluoride concentrations in urine were found to be appreciably high. The victims suffered abnormally high alkaline phosphatase and high values of AST (GOT) but low calcium levels in serum leading to calcium loss, renal insufficiency, vitamin D deficiency and bone diseases of low to severe magnitudes. Efforts have been made to throw light on structural changes of water due to fluoride contamination and other related aspects.

Keywords: Clinical aspects, fluoride contamination, ion chromatography, Nalhati (West Bengal), structural changes of water.


Novel synthesis of some N-glycosyl benzimidazolyl thiocarbamides and their antimicrobial activity

Samidha S. Kadu*a, Gajanan V. Korpea and R. P. Karyakarteb

aP.G. Department of Chemistry, Shri Shivaji College, Akola-444 001, Maharashtra, India
E-mail: samidhakadu@gmail.com
bDepartment of Microbiology, Govt. Medical College, Akola-444 001, Maharashtra, India

Manuscript received online 25 July 2015, accepted 09 August 2016

Abstract: Several 1-peracetyl and perbenzoyl glycosyl benzimidazolyl thiocarbamides were synthesized by the interaction of peracetyl and perbenzoyl glycosyl isothiocyanate and 2-amino benzimidazole. The identities of these newly synthesized compounds were established on the basis of usual chemical transformations and IR, 1H NMR and Mass spectral studies. All the synthesized compounds have been evaluated for their antibacterial and antifungal activity against different bacteria and fungi by agar diffusion method.

Keywords: Glycosyl isothiocyanate, aminobenzimidazole, benzimidazolyl thiocarbamide, antimicrobial activity.


Synthesis, characterization and antifungal activity of thiosemicarbazides and thiosemicarbazones

Sukesha Joshi*a, Sunita Sharma*b and Geetika Arora*a

aDepartment of Chemistry, Punjab Agricultural University, Ludhiana-141 004, Punjab, India
E-mail: joshisukesha@gmail.com, geetu2487@yahoo.com
bDepartment of Plant Breeding and Genetics, Punjab Agricultural University, Ludhiana-141 004, Punjab, India, E-mail: sunita_sharma@pau.edu

Manuscript received online 02 June 2016, accepted 24 September 2016
Abstract: Thiosemicarbazides (1, 2 and 3) were synthesized by reacting aniline with carbon disulfide followed by addition of hydrazine or phenyl hydrazine or 2,4-dinitrophenyl hydrazine respectively. Different substituted benzaldehydes were condensed with 4-phenylthiosemicarbazide to afford respective thiosemicarbazones (4-15). Antifungal activity of the synthesized compounds exhibited that thiosemicarbazides were more effective than thiosemicarbazones against Macrophomina phaseolina and Fusarium moniliforme. All the synthesized compounds registered less activity than bavistin against both fungi at all concentrations.

Keywords: Thiosemicarbazides, hydrazine derivatives, thiosemicarbazones, antifungal activity, ED50.


Hemidesterpene, a new triterpenoid from Hemidesmus indicus R.Br. root

Avijit Banerjia,ab, Julie Banerjib, Manosi Das a and Jairam Hazraca

aNational Research Institute of Ayurvedic Drug Development, Kolkata-700 091, India
bRetired Professor of Chemistry, University of Calcutta, Kolkata-700 009, India
E-mail: ablabcu@yahoo.co.uk

Manuscript received 29 September 2016, accepted 19 October 2016

Abstract: Chemical investigation of Hemidesmus indicus roots yielded α-amyrin acetate, β-amyrin acetate, taraxesteryl acetate and a new triterpenoid designated hemidesterpene. The latter was characterised as Δ12,13-taraxesteryl acetate from spectroscopic investigations.

Keywords: Anantamul, Hemidesmus indicus, triterpenoids, hemidesterpene, Δ12,13-taraxesteryl acetate.

J. Indian Chem. Soc., Vol. 93, December 2016, pp. 1405-1411

Electrochemical detection of fluoride in water using polymer encapsulated Zr-EDTA-PCV reagent

Kakoli Dutta and Priyabrata Sarkar*

Department of Polymer Science and Technology, University of Calcutta, Kolkata-700 009, India
E-mail: kakoli_mukherjee@yahoo.com, sarkarpriya@gmail.com Fax: 91-33-24852976

Manuscript received 28 July 2016, revised 17 October 2016, accepted 20 October 2016

Abstract: Long term exposure to fluoride leads to development of fluorosis in dental, skeletal and non-skeletal forms. Thus its detection by sensitive and reliable method is an urgent need. In this paper, an electrochemical sensor was reported for potentiometric detection of fluoride. The methodology included preparation of a colored paste by mixing stipulated quantity of pyrocatechol violet (PCV), zirconium oxychloride (ZrOCl2) and ethylene diamine tetra acetic acid (EDTA) followed by its in situ entrapment in a polymeric membrane made of poly vinyl alcohol (PVA) and gelatin crosslinked with glutaraldehyde on the surface of a working electrode. When the polymer modified electrode was dipped in fluoride contaminated water, a distinct change in potential was observed with concentration of fluoride. The electrochemical impedance spectroscopy (EIS) was also used to detect fluoride. Both potentiometry and EIS methods were found fruitful in addressing the problem of measurement of fluoride contaminated drinking water. The LOD of the sensor was found to be 0.325 ppm and sensitivity 7 mV/ppb.

Keywords: Fluoride, fluorosis, polymer-electrode, sensor, potentiometry, EIS.
Synthesis and biological evaluation of 4-aryl-5-hepta-\textit{O}-benzoyl-\textit{\textbeta\textbeta}\textit{\textbeta}\textit{\textbeta}-\textit{D}-lactosylimino-3-hepta-\textit{O}-benzoyl-\textit{\textbeta\textbeta}\textit{\textbeta}\textit{\textbeta}-\textit{D}-lactosylimino-1,2,4-dithiazolidines (hydrochlorides)

Kavita M. Heda\textsuperscript{a} and Shirish P. Deshmukh\textsuperscript{b}

\textsuperscript{a}Department of Chemistry, Shri R. L. T. College of Science, Akola-444 001, Maharashtra, India
E-mail: kavitaheda25@gmail.com

\textsuperscript{b}P.G. Department of Chemistry, Shri Shivaji College, Akola-444 001, Maharashtra, India

\textit{Manuscript received 04 November 2015, accepted 26 October 2016}

\textbf{Abstract} : A series of 4-aryl-5-hepta-\textit{O}-benzoyl-\textit{\textbeta\textbeta}\textit{\textbeta}\textit{\textbeta}-\textit{D}-lactosylimino-3-hepta-\textit{O}-benzoyl-\textit{\textbeta\textbeta}\textit{\textbeta}\textit{\textbeta}-\textit{D}-lactosylimino-1,2,4-dithiazolidines (hydrochloride) have been synthesized by the interaction of various 1-hepta-\textit{O}-benzoyl-\textit{\textbeta\textbeta}\textit{\textbeta}\textit{\textbeta}-\textit{D}-lactosyl-3-aryl thiocarbamides with \textit{N}-hepta-\textit{O}-benzoyl-\textit{\textbeta\textbeta}\textit{\textbeta}\textit{\textbeta}-\textit{D}-lactosyl-5-chloro isothiocarbamoyl chloride. These compounds were screened for their antibacterial and antifungal activities against \textit{E. coli}, \textit{P. vulgaries}, \textit{S. aureus}, \textit{S. typhimurium}, \textit{K. pneumoniae}, \textit{Ps. aeruginosa}, \textit{A. niger} and \textit{C. albicance}. The newly synthesized compounds have been characterized by analytical and IR, \textsuperscript{1}H NMR and Mass spectral studies.

\textbf{Keywords} : Lactosyl thiocarbamides, hepta-\textit{O}-benzoyl-\textit{\textbeta\textbeta}\textit{\textbeta}\textit{\textbeta}-\textit{D}-lactosyl-5-chloro isothiocarbamoyl chloride, 1,2,4-dithiazolidines, antimicrobial activity.