

Kinetics and mechanism of oxidation of quinol, ascorbic acid and hydrogen peroxide by $[\text{Mn}_2^{\text{IV}}(\text{m-O})_2(\text{phen})_4]^{4+}$ ion[†]

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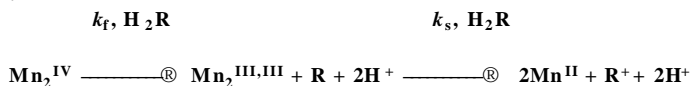
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Abstract : The oxo-bridged dimanganese(IV,IV) complex, $[\text{Mn}_2^{\text{IV}}(\text{m-O})_2(\text{phen})_4]^{4+}$, $\{1\}^{4+}$ (phen = 1,10-phenanthroline) forms metastable solutions in dilute nitric acid media, where its UV-Vis spectra do not degrade for ~20 min. This solution quantitatively oxidizes ascorbic acid, quinol and hydrogen peroxide to dehydroascorbic acid, quinone and oxygen respectively. In general, each mole of the oxidant consumes two moles of reducing agent (H_2R), but stoichiometry depends on initial $[\text{H}_2\text{O}_2]$. Under the first order conditions, maintained with excess (H_2R), a two-step irreversible consecutive kinetics leads the oxidant itself to Mn^{II} , at a rate much faster than auto-decomposition of the complex :



Among all the three H_2R , hydrogen peroxide reacts slowest. When H_2O_2 is added in low concentrations, some of the intermediate Mn_2^{III} are lost via auto-decomposition before advancing to the second (k_s) step and thus affects the stoichiometry. Protonated oxidants are more reactive than their conjugate bases, Mn_2^{IV} is more reactive than Mn_2^{III} and reactivity order of the reducing agents is : $\text{H}_2\text{A} \approx \text{H}_2\text{Q} \gg \text{H}_2\text{O}_2$. These observations are consistent with an outer sphere mechanism. The k_f step for ascorbic acid exhibits significant solvent isotope effect indicating an electroprotic process to be the rate-determining step of this path.

Keywords : Manganese(IV) oxidation, quinol, ascorbic acid, hydrogen peroxide, kinetics and mechanism.

Ionic liquid promoted regio - and stereoselective addition of thiols to alkynes and alkenes under organic solvent free condition – A green reaction[†]

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Abstract : A simple ionic liquid, 1-methyl-3-pentylimidazolium fluoroborate, $[\text{pmIm}]\text{BF}_4$, promotes *anti*-Markovnikov addition of thiols to alkynes providing (*Z*)- and (*E*)-vinyl sulfides stereoselectively. The addition of thiols to alkenes in presence of another ionic liquid, $[\text{pmim}]\text{Br}$ proceeds through *anti*-Markovnikov manner, whereas the addition to vinyl ethers and acetates occurs at more electrophilic C-2 position adjacent to oxygen. The products are obtained in high yields.

Keywords : Green chemistry, ionic liquid, thiols, alkyne, alkene.

Microwave-assisted solvent-free synthesis of some bio-active substituted dihalo 1,4-benzoquinones on silica gel solid support[†]

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Abstract : An environmentally benign solvent-free microwave-assisted synthesis of biologically active 2,5-diarylamino-3,6-dihalo-1,4-benzoquinones by the condensation of substituted anilines and chloranil has been reported on the inorganic solid support of silica gel.

Keywords : Microwave irradiation, solvent-free synthesis, silica gel solid support, dihalo 1,4-benzoquinones.

Water vapour adsorption by L-amino acids at different water activities[†]

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Abstract : Experimental studies on the hydration of all 20 L-amino acids by isopiestic vapour pressure method have been carried out in detail. The water vapour adsorption curves of these amino acids resemble type II or type III BET isotherms. The maximum water uptake (Dn_1^0) of the amino acids at relative humidity equal to unity and values of secondary hydration (n_1^s) of these amino acids at p/p_0 equal to 0.92 have been compared critically with each other. Values of Dn_1^0 and n_1^s for each amino acid has been found to be different from that of the corresponding amino acid residue obtained from our earlier studies. It appears that many amino acids having hydrophobic side chain may form crystals with strong ionic bonds so that they resist hydration at 0.92 relative humidity. The standard free energies of hydration of all amino acids at p/p_0 equal to unity have been evaluated using the Bull equation. The activity coefficients of several amino acids having low solubilities at p/p_0 close to unity has been evaluated when hydrated mixtures remain in gel state.

Keywords : L-Amino acids, adsorption, polypeptides, thermodynamic parameters, hydration of amino acids.

Heterocyclization of some chalcones to isoxazoles, pyrazoles and pyrimidine nuclei under microwave irradiation and their biological profile[†]

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Abstract : Rapid and efficient methods for the preparation of a set of isoxazole, pyrazole and pyrimidine derivatives of imidazolinone and quinazolinone by the reaction of 5-substituted arylidene {2-(imidazolyl/quinazolyl)imino}thiazolidinone (chalcones) with hydroxylamine, urea and hydrazine hydrate under MWI are reported. Excellent yields and higher purity are obtained in MW enhanced synthesis as compared to the conventional procedure which required exceedingly long reaction times, high temperatures and tedious workups. The potent antimicrobial effects of the synthesized compounds were investigated.

Keywords : Chalcones, isoxazoles, pyrazoles, pyrimidines, thiazolidinones.

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Antioxidant and other beneficent effects of free and conjugated phytosteroids of *Solanum* and *Withania*[†]

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Abstract : Antioxidant capacity of an array of free and conjugated phytosteroids of *Solanum xanthocarpum* and *Solanum nigrum*, and withasteroids of *Withania somnifera* has been assessed. Four standard sets of assays, namely, reduction of ABTS, DPPH, FRAP and superoxide radical, have been used. The contribution, in this regard, of metal ions, naturally-complexed with the phytosteroids and withasteroids, has also been evaluated. The findings suggest the contribution of naturally occurring metallo-organic complexes in human well being. The mechanisms suggested for the antioxidant actions of the compounds project the role of molecular architecture of free and conjugated steroids. Some other beneficent actions of these compounds, e.g. systemic lowering of cholesterol and LDL, and the selective inhibition of COX-2 by sitoindoside-indolealkylamine-conjugated withasteroids, are noteworthy. The last-named compound(s) contribute also to the adaptogenic activity of *W. somnifera*.

Keywords : *Solanum*, *Withania*, phytosteroids, withasteroid-indolealkylamine, metal ion conjugates, antioxidant capacity, adaptogen.

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Applications of polychelates of 4-substituted benzophenone based resins with 'd' and 'f' block elements[†]

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Contents :

1. Introduction
2. Benzophenone based resins
 - 2.1. Preparation of 4-substituted benzophenone derivatives
 - 2.2. Benzophenone-formaldehyde resin

2.3. *Benzophenone-diol resins*

2.4. *4-Methacryloxy benzophenone resins*

3. Polychelates

3.1. *Polychelates with transition metal ions*

3.2. *Polychelates with lanthanide metal ions*

4. Catalytic activity

5. Antimicrobial activity

6. Conclusion

7. References

Keywords : Polychelates, substituted benzophenone, 'd' block elements, 'f' block elements.

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Determination of the absolute values of Gibbs energy of hydration or solvation $DG^0_{\text{abs}}(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ of monovalent (alkali metal and halide) ions and other thermodynamic parameters in aqueous and non-aqueous solvents using a single standard state and analysis of $DG^0_{\text{abs}}(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ values based on cluster-ion solvation method[†]

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Abstract : Absolute values of Gibbs energy of hydration (h) or solvation (s) of alkali metal and halide ions $DG^0_{\text{abs}}(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ and other thermodynamic parameters in aqueous and non-aqueous solvents (methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, ethylene glycol, propylene carbonate (PC), *N*-methyl formamide (NMF), acetone, tetrahydrofuran (THF), 1,4-dioxan, acetonitrile) were determined directly using modified Born equation and a single standard state [i.e. DG^0 and DH^0 (but not DS^0) of H_2 gas and other elements to be zero in their elementary standard states at 1 atm. pressure (1 bar) and 298 K]. The $DH^0_{\text{abs}}(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ and $DG^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ values are calculated considering ion-dipole, ion-quadrupole interactions and without considering the interaction terms. Very few data are available in non-aqueous solvents for comparison. Most of the single ion values (particularly for the anions) suffer from limitations associated with the erroneous principle of division of solvation energies $DG^0_{\text{h or s}}(\text{MX})$ or $DH^0_{\text{h or s}}(\text{MX})$ of electrolytes into single ion values.

$DG^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{h}}$ values determined using cluster-ion solvation data have also been presented. The values have been claimed to be most accurate in recent years. However, the method involves a number of assumptions of doubtful validity and the values cannot be regarded to be equivalent to $DG^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ determined by other workers using different methods.

Coupling the values of $DG^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ and $DH^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{h or s}}$ with $DG^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{g}}$ and $DH^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{g}}$ values in the gaseous state, $DG^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{water or org. solvent}}$, $DH^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{water or org. solvent}}$ and $DS^0(\text{M}^+ \text{ or } \text{X}^-)_{\text{water or org. solvent}}$ [values in water and in organic solvents] are determined.

Keywords : Alkali metal ions, aqueous solvent, absolute values : enthalpy and Gibbs energy of hydration or solvation of ions, Born equation or modified Born equation, cluster-ion solvation, electron affinity (EA), halide ions, ionic additivity, ion-dipole interactions, ion-quadrupole interactions, ionization potential (IP), non-aqueous solvent.

Use of modified ZnS in photocatalytic bleaching of eosin Y[†]

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Abstract : The photocatalytic activity of zinc sulphide has been enhanced using potassium chloride on heating at various temperatures. The sample was mixed with KCl in certain molar ratio i.e. 0.25. The progress of the reaction was monitored spectrophotometrically. The effect of various operating parameters like pH, concentrations of dye, amount of semiconductor, light intensity etc. on the rate of photocatalytic bleaching of eosin Y was observed. More efficient ZnS as photocatalyst was found at 673 K for 3.0 h under muffle furnace. A tentative mechanism for the photocatalytic bleaching of the dye has also been proposed.

Keywords : Zinc sulphide, eosin Y, molar ratios, photocatalytic activity.

Global Warming – The Debate of the Century[†]

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Abstract : Global warming is an environmental issue of deep concern all over the world. It is centred around greenhouse gases mainly carbon dioxide. It has the potential to rival nuclear wars in terms of irreversible damage to the environment. The greenhouse gases can be arranged in a sequence in terms of global warming potential (GWP) – CFC > N₂O > CH₄ > CO₂. The United Nations is seized with the issue – the various agencies – UNDP, IPCC etc. have recommended several measures for curtailment of greenhouse gas emissions. The IVth Assessment Report of IPCC on Global Warming (2007) is significant – the award of Nobel Peace Prize for the work of the Panel (2007) is likely to set at rest all the controversies in respect of global warming.

Keywords : Global warming, solar energy, greenhouse gases, carbon dioxide.

Structure-reactivity correlation in the oxidation of substituted benzaldehydes by 2,2'-bipyridinium chlorochromate[†]

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Abstract : Oxidation of thirty six monosubstituted benzaldehydes by 2,2'-bipyridinium chlorochromate (BPCC) in dimethylsulphoxide (DMSO), leads to the formation of corresponding benzoic acids. The reaction is of first order with respect to both BPCC and aldehydes. The reaction is promoted by hydrogen ions; the hydrogen ion dependence has the form $k_{obs} = a + b[H^+]$. The oxidation of [²H]benzaldehyde (PhCDO) exhibited a substantial primary kinetic isotope effect. The reaction was studied in nineteen different organic solvents and the effect of solvent was analysed

using Taft's and Swain's multi-parametric equations. The rates of the oxidation of *para*- and *meta*-substituted benzaldehydes showed excellent correlation in terms of Charton's triparametric LDR equation, whereas the oxidation of *ortho*-substituted benzaldehydes were correlated well with tetraparametric LDRS equation. The oxidation of *para*-substituted benzaldehydes is more susceptible to the delocalized effect than is the oxidation of *ortho*- and *meta*-substituted compounds, which display a greater dependence on the field effect. The positive value of ρ suggests the presence of an electron-deficient reaction centre in the rate-determining step. The reaction is subjected to steric acceleration by the *ortho*-substituents. A suitable mechanism has been proposed.

Keywords : Oxidation, 2,2'-bipyridinium chlorochromate, substituted benzaldehydes, correlation studies.

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Micelles : A short review[†]

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Abstract : Micelles are formed when surfactants are dissolved in water. The micelles are clusters of surfactant molecules with definite shapes and sizes. However the shape and size of the micelle are functions of the nature of the system. It is generally accepted that micelle formation is entropy dominated. There are theories to explain the formation of clusters, their shapes and their sizes. In this short review some of the theories and experimental results are discussed though no attempt has been made for a comprehensive review of the literature.

Keywords : Micelles, size, shape, theory.

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Effect of surfactant chain length of cationic micelles of alkyl trimethyl ammonium bromides (C_nTAB) on the spectroscopic properties of 2-anthracene sulphonate[†]

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Abstract : The emission properties of 2-anthracene sulphonate (2-AS) have been studied in cationic micellar media of alkyl trimethyl ammonium bromides (C_nTAB) of varying chain lengths. The effect of chain length of the cationic surfactants on the binding constant values of 2-AS with the micelles has been determined. The location of the probe molecule within the micelles has been ascertained from the emission characteristics of the probe in the presence of the micelles and comparing with that in dioxan-water mixture of varying composition.

Keywords : Fluorescence, polarity, exciplex, binding constant, chain length.

Production of solar hydrogen through photocatalysis by CdS and CdS/ZnS modified by Pt, Ag₂S and Si[†]

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Abstract : Photocatalytic production of solar hydrogen using CdS suspensions in aqueous solution containing Na₂S-Na₂SO₃ has been studied. CdS prepared from different sources show different photocatalytic activity towards generation of hydrogen. CdS alone as well as modified by doping materials such as Pt, Ag₂S and Si and mixing with ZnS has been investigated. When unmodified CdS is mixed with ZnS, the photocatalytic efficiency of CdS is enhanced and becomes maximum at a particular composition. When CdS is doped, the efficiency increases and in each case the best result is obtained at different particular composition.

Keywords : Photocatalysis, solar energy, hydrogen, Cd S.

Agrostophyllanthrol and isoagrostophyllanthrol, two novel diastereomeric phenanthropyran derivatives from the orchid *Agrostophyllum khasianum*[†]

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Abstract : Agrostophyllanthrol and isoagrostophyllanthrol, two novel diastereomeric phenanthropyran derivatives were isolated from the orchid *Agrostophyllum khasianum* which earlier afforded eleven stilbenoids, viz. the two dimeric phenanthrene derivatives agrostonin [2,2 ζ ,7,7 ζ -tetrahydroxy-4,4 ζ ,6,6 ζ -tetramethoxy-1,1 ζ -biphenanthryl] and agrostonidin [2,2 ζ ,6,6 ζ -tetrahydroxy-4,4 ζ ,7,7 ζ -tetramethoxy-1,1 ζ -biphenanthryl], eight phenanthropyran derivatives imbricatin [2,7-dihydroxy-6-methoxy-9,10-dihydro-5H-phenanthro[4,5-*bcd*]pyran], agrostophyllidin [7-hydroxy-2,6-dimethoxy-9,10-dihydro-5H-phenanthro[4,5-*bcd*]pyran], agrostophylloxidin [7-hydroxy-2,5,6-trimethoxy-5H-phenanthro[4,5-*bcd*]pyran], flaccidin [2,6-dihydroxy-7-methoxy-5H-phenanthro[4,5-*bcd*]pyran-5-one], isoflaccidin [2,7-dihydroxy-6-methoxy-5H-phenanthro[4,5-*bcd*]pyran-5-one], agrostophyllin [7-hydroxy-2,6-dimethoxy-5H-phenanthro[4,5-*bcd*]pyran], agrostophyllone [7-hydroxy-2,6-dimethoxy-5H-phenanthro[4,5-*bcd*]pyran-5-one], agrostophylloxin [2,6,7-trimethoxy-5H-phenanthro[4,5-*bcd*]pyran-5-one] and the bibenzyl derivative moscatalin [4,4 ζ -dihydroxy-3,3 ζ ,5-trimethoxybibenzyl]. The structures of agrostophyllanthrol and isoagrostophyllanthrol were established as 7-hydroxy-2,6-dimethoxy-5H-phenanthro[4,5-*bcd*]pyran-5(equat)ol and 7-hydroxy-2,6-dimethoxy-5H-phenanthro[4,5-*bcd*]pyran-5(ax)ol, respectively from various spectral and chemical evidence. Agrostophyllanthrol and isoagrostophyllanthrol, thus, represent two novel examples of otherwise conformational isomers becoming highly stable diastereomers due to unusual steric hindrance to conformational flipping.

Keywords : *Agrostophyllum khasianum*, Orchidaceae, agrostophyllanthrol and isoagrostophyllanthrol, phenanthropyran derivatives, otherwise conformational isomers becoming stable diastereomers, steric hindrance to conformational flipping.

Spectrophotometric study of a charge transfer complex of 4 - acetamidophenol with 2,3 -dichloro-1,4-naphthoquinone in pure ethanol medium[†]

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Abstract : 2,3-Dichloro-1,4-naphthoquinone has been found to form a charge transfer complex with 4-acetamidophenol (paracetamol). The charge transfer band has been located and the formation constant value at different temperatures have been measured by using the Benesi-Hildebrand equation modified for a 2 : 1 complex. Thermodynamic quantities, the enthalpy and entropy of formation of the complex have been obtained from the temperature dependence data. The sign and magnitude of these quantities have been discussed.

Keywords : 2,3-Dichloro-1,4-naphthoquinone, paracetamol, charge transfer or electron donor-acceptor complex, 2 : 1 complex, enthalpy and entropy of complex formation.