

45 Years of Nickel Hydride

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The history of discovery of nickel hydride and studies of its properties is briefly described. Nickel hydride, obtained firstly on electrochemical way, was then synthesized directly from elements under high pressure of gaseous hydrogen. This was the first high pressure synthesis of a metal hydride, which opened a novel and very fruitful field of inorganic synthesis. It was the foundation for discovery of new materials and new phenomena.

Key words: nickel hydride, high pressure

The Synthesis and Spectral Characterization of Complexes of Co(II), Ni(II), Cu(II) and Zn(II) with a New 1,3-Dioxolane Derivatives of Unsymmetrical *vic*-Dioximes

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Two new *vic*-dioxime ligands containing 1,3-dioxolane ring and ethylenediamine, *N*-hydroxy-2-(hydroxyimino)-*N*-(2-[(2-phenyl-1,3-dioxolan-4-yl)methyl]amino)ethyl)ethanimidamide (L^1H_2), *N*-hydroxy-2-(hydroxyimino)-*N*-(2-[(2-methyl-2-phenyl-1,3-dioxolan-4-yl)methyl]amino)ethyl)ethanimidamide (L^2H_2) and their complexes have been prepared from chloride salts of Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} in EtOH. The authenticity of the ligands and their complexes have been established by IR, 1H - and ^{13}C -NMR spectra, UV-Visible spectroscopy, elemental analysis and magnetic susceptibility measurements. The complexes are mononuclear. Ligands form complexes $[(L^1H)_2M]$ and $[(L^2H)_2M]$ with a metal:ligand ratio of 1:2 with $M = Co^{II}$, Ni^{II} and Cu^{II} . Zn^{II} forms with ligands complexes $[(Zn)(L^1H)(Cl)(H_2O)]$ and $[(Zn)(L^2H)(Cl)(H_2O)]$ which have a metal:ligand ratio of 1:1. The mononuclear Co^{II} , Ni^{II} and Cu^{II} complexes indicated that the metal ions are coordinated to ligands by two N atoms, as do most of the *vic*-dioximes. In the $Zn(II)$ complexes the ligands are coordinated by the N and O atoms of the *vic*-dioximes.

Key words: dioximes, transition metals, synthesis of *vic*-dioxime complexes

Synthesis and Physico-Chemical Studies of 14-Membered Tetraazamacrocyclic Complexes of Co(II), Ni(II), Cu(II) and Zn(II) Derived from 3,4-Diaminobenzophenone

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A new series of 14-membered tetraazamacrocyclic complexes [MLX₂] (M = Co(II), Ni(II), Cu(II), and Zn(II), X = Cl or NO₃) have been synthesized by the condensation reaction of 3,4-diaminobenzophenone with 1,3-dibromopropane in the presence of metal ions as templates in methanol as solvent. The macrocyclic complexes have been characterized on the basis of elemental analysis, IR, ¹H NMR, EPR, UV-visible, magnetic susceptibility and conductivity measurements at room temperature. An octahedral geometry has been proposed for all of the complexes where two coordination sites are occupied by Cl or NO₃ and the other four sites by secondary amine. The low conductivity data suggests their non-ionic nature.

Key words: tetraazamacrocyclic complexes, octahedral geometry, 3,4-diaminobenzophenone, 1,3-dibromopropane, condensation reaction

Hydrogen Peroxide Oxidation of Mono- and Disubstituted Alkylarenes Catalyzed by Dinuclear $\text{Co}^{\text{III}}-\text{Cu}^{\text{II}}$ Macrocyclic Complex

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C–H oxidation of anthracene and eight other alkylarenes with binuclear macrocyclic complex of $\text{Co}^{\text{III}}-\text{Cu}^{\text{II}}$ as a catalyst in the presence of 30% aqueous hydrogen peroxide to the corresponding carbonyl compounds were studied. The oxidation took place selectively at the benzylic C–H bond and no oxidation was observed in aromatic ring. The reaction is simple, clean and high yielding and generates water as the only by-product.

Key words: monosubstituted arenes, disubstituted arenes, oxidation, hydrogen peroxide, catalyst, selective oxidation, binuclear macrocyclic complex

Spectral Properties and DNA-binding Study of 6a,12a-Diazadibenzo-[a,g]fluorenylium Derivative

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The DNA binding affinity and anion effect on the aggregation of a G-quadruplex selective ligand, 6a,12a-diazadibenzo-[a,g]fluorenylium derivative, were studied by UV-Vis absorption, molecular modeling and fluorescence spectroscopy. The anion character and its concentration influenced the spectral properties of ligand aggregates. Observed spectral peculiarities were discussed in terms of the formation of H- and J-type aggregates. The DNA binding mode and affinity of the ligand depended on the salt concentration; preferential binding to G-quadruplex DNA was clearly seen at higher salt concentration.

Key words: aggregation, fluorescence, fluorenylium derivative, DNA binding, G-quadruplex DNA, intercalation

Simple Synthesis of Dialkyl 2-(3-Oxo-3*H*-indol-2-yl)-but-2-enedioates

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Triphenylphosphine undergoes a smooth addition reaction with dialkyl acetylenedicarboxylates in the presence of isatin or 5-bromoisatin to produce stable crystalline phosphorus ylides. These products exist as a mixture of two geometrical isomers. Dynamic NMR effects have been observed in the ¹H NMR spectra of dimethyl 2-(2,3-dioxo-2,3-dihydro-1*H*-indol-1-yl)-3-(1,1,1-triphenyl-λ³-phosphanylidene)succinate. These ylides are converted to dialkyl 2-(3-oxo-3*H*-indol-2-yl)-but-2-enedioates in boiling toluene.

Key words: isatin, indole derivatives, triphenylphosphine, intramolecular Wittig reaction

Mechanistic and Kinetic Study of Free Radical Polymerization Photoinitiated by Xanthene Dye – N-Phenylglycine Derivatives Photoredox Pairs

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The mechanistic and free radical photopolymerization kinetic studies for the selected xanthene dyes in the presence of N-phenylglycine derivatives are described. The examined transient phenomena, using nanosecond laser flash photolysis, confirm that the oxidation of N-phenylglycine derivatives is a one electron transfer process. The laser flash measurements as well as the steady-state experiments allowed to establish the structure of a free radical, which in ethyl acetate-DMF (9:1) solution, is mostly formed after the electron transfer, *e.g.* N-phenylglycine α -aminoalkyl radical (Ph-NH-C^{*}(H)-COOH). However, a careful analysis of the photolysis products indicates another path of secondary reactions that includes the decarboxylation of N-phenylglycine N-centered radical cation, yielding Ph-NH-CH₂^{*} radical. The measured electron transfer rates oscillate from 0.23×10^8 to $35.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ that, in turn, suggests the possibility that the electron transfer process might control the rate of photoinitiated polymerization. The comparison of the rates of xanthene dye triplet state quenching and the measured rates of polymerization shows, however, that there is no correlation between these two variables. This observation permits to conclude that the rate of photopolymerization is probably controlled by the secondary processes such as: (i) the rate of proton transfer reaction between N-phenylglycine radical cation and xanthene dye radical anion, (ii) the participation of decarboxylation process in the secondary reactions and (iii) the reactivity of the free radicals obtained after electron transfer.

Key words: xanthene dyes, photoreduction N-phenylglycine derivatives, photooxidation, mechanistic study, kinetic study, photoinitiation of free radical polymerization

Functionalized Imidazolium Salt Based Ionic Liquids

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A new series of task-specific ionic liquids (TSILs) have been prepared. They are based on the 1-alkylthiomethyl-3-methylimidazolium and 1-alkylthiomethyl-3-butoxy-methylimidazolium cations with anions such as BF_4^- , NTf_2^- , CF_3CO_2^- and $(\text{CN})_2\text{N}^-$. Their physical properties (density, viscosity, solubility and thermal stability) have been estimated. All TSILs can be decomposed by oxidation using KMnO_4 in an aqueous solution. The alkylthiomethyl group distinguishes these liquids from other TSILs by the fact that the former can be utilizing ozonation in an aqueous solution as a means of destruction.

Key words: task-specific ionic liquids, imidazolium salts, ozonation

Isothermal Gas Chromatographic Partition Coefficients of n-Alkanes, Benzene, Methylbenzenes and Chlorobenzenes on Two Opposite Polarity Stationary Phases

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Partition coefficients of benzene, its twelve methylbenzenes and its twelve chlorobenzenes have been estimated on two fused silica capillary columns coated with the stationary phases HP-5 and ZB-WAX at 100–180°C range. These retention data are compared to evaluate the column temperature effect, the dependence of the substituent number and the influence of the stationary phase polarity. The partition coefficient decreases with increasing column temperature in all cases, but, on the contrary, it increases with the number of methyl radicals and chlorine atoms at each stationary phase at each temperature, and it increases for the polar stationary phase. The partition coefficients of the isomers (1,2-), (1,2,3-) and (1,2,3,4-) are larger than those of the other diisomers (1,3-) and (1,4-), triisomers (1,2,4-) and (1,3,5-), and tetraisomers (1,2,3,5-) and (1,2,4,5-). Discussion in terms of physicochemical properties of these isomers is forwarded.

Key words: gas chromatography, n-alkanes, benzene and methyl and chloroderivatives, partition coefficients, effects of column temperature, stationary phase and nature of the substituent

Effect of Initial N,N'-Methylene Bisacrylamide Concentration on the Swelling Behaviour of Acrylic-based Superabsorbent Polymers

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A series of superabsorbent polymers based on acrylic acid has been synthesized by a solution polymerization technique at 60°C. The effect of the N,N'-methylene bisacrylamide concentration on the swelling behaviour of these hydrogels in deionized water and saline solution was investigated. Experimental results indicate that the absorbance in deionized water or saline solution decreases on increasing the concentration of crosslinker. Moreover, the amount of swelling in 0.2 wt% NaCl_(aq) is smaller than that in deionized water, a result that is due to the decrease in the osmotic pressure (ionic pressure) difference between polymer and external solution at high ionic strength. High swelling and appropriate absorption kinetics can be obtained by altering parameters such as initial monomer concentration, range of neutralization, temperature, initiating system and range of crosslinker concentration. These changes were studied but are not reviewed here. Rates of swelling for these absorbents were found to fit the Voigt expression. Relationships were also established between the ultimate degree of swelling and the ratio of crosslinker to monomer. The results of the investigation involving water or saline solution diffusion in hydrogels approximate to Case II sorption in the early stages of the swelling process and to Case I in the later stages.

Key words: superabsorbents, swelling behaviour, acrylic acid, crosslinking

Thermodynamics and Kinetics of Point Defects in Nonstoichiometric Nickel Oxide

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The deviation from stoichiometry and chemical diffusion in metal-deficient nickel oxide have been studied as a function of temperature (1073–1673 K) and oxygen pressure ($10\text{--}10^5$ Pa), using microthermogravimetric techniques. It has been found that the nonstoichiometry, y , in Ni_{1-y}O is the following function of temperature and equilibrium

oxygen pressure: $y = 0.153 \cdot p_{\text{O}_2}^{1/6} \cdot \exp\left(-\frac{80\text{kJ/mol}}{RT}\right)$ clearly indicating that the predominant

defects in this oxide are non-interacting, doubly ionised cation vacancies and electron holes randomly distributed in the crystal lattice. Re-equilibration rate measurements of nonstoichiometry have shown that the vacancy diffusion coefficient, D_V , being the direct measure of defect mobility, does not depend on their concentration and is the following

function of temperature: $D_V = 0.062 \cdot \exp\left(-\frac{152\text{kJ/mol}}{RT}\right)$ Using both these results the

self-diffusion coefficient of cations, D_{Ni} , in Ni_{1-y}O has been calculated as a function of T

and $p(\text{O}_2)$: $D_{\text{Ni}} = 9.49 \cdot 10^{-3} \cdot p_{\text{O}_2}^{1/6} \cdot \exp\left(-\frac{232\text{kJ/mol}}{RT}\right)$ being in excellent agreement with experimental results obtained on single crystalline material.

Key words: nickel oxide, nonstoichiometry, diffusion

A Study of Photocatalytic Oxidation of Indanthrene Red LGG an Anthraquinone Vat Dye on TiO₂

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Nanometer-sized powder of TiO₂ is prepared by chemical methods of gel to crystalline conversion. The crystallite sizes obtained are in the range of 160 Å to 180 Å, as estimated by Scanning Electron Microscopic (SEM) and X-ray diffraction studies. The photocatalytic activity of this powder in the mineralization of Indanthrene Red LGG is evaluated. The maximum photocatalytic activity is observed in the system, in which the photocatalyst is used in the presence of an oxidizing agent. The effect of inorganic oxidizing species to act as an electron scavenger, thus, influencing the rate of photocatalytic degradation, is studied. Extent of degradation is followed by UV-visible and IR spectroscopy. Based on the results, a kinetic model for the degradation is proposed.

Key words: semiconductor photocatalyst, indanthrene red, spectroscopy, photodegradation

Kinetics and Mechanism of Metal Cation Catalysis in the Hydrolysis of p-Nitrophenyl Picolinate (PNPP)

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The hydrolysis of PNPP was investigated in the presence and absence of Co(II), Cu(II), Ni(II), Zn(II), La(III) at 25°C and ionic strength of 0.1 mol dm⁻³. The results indicate that the spontaneous hydrolysis of PNPP was catalyzed by hydronium ion, hydroxide ion and water molecule, because of the existence of the pyridium nitrogen, while the metal ion catalyzed hydrolysis of PNPP at zero buffer concentration fulfills the equation:

$$k_{obsd} = \frac{K_a}{[H^+] + K_a} \left(k_H [H^+] + k_0 + \frac{k_{OH} K_w}{[H^+]} \right)$$

showing that the reaction proceeds *via* nucleophilic attack by external OH⁻ on the metal ion complex of PNPP. The order of catalytic ability of different metal ions was interpreted by the stability of the complex structure relative to the structure of the ground-state intermediate, employing the method devised by Kurz for catalyzed reaction.

Key words: metal ion, catalysis, PNPP, kinetics and mechanism

**The Homogeneous Synthesis of N₂O in
Ammonia Oxidation Process**

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Plasma Conversion of Methane in Spouted Bed

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