Reactions of Chlorinated Pyrimidine Derivatives with Carbanions Bearing Nucleophugal Groups at the Carbanionic Center

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(Received January 13th, 2000; revised manuscript June 16th, 2000)

Reactions of chloro-, dichloro-, and trichloropyrimidines with carbanions bearing leaving groups at the carbanionic center are described. 2-Chloropyrimidine and 2,4-dichloropyrimidine react at low temperature with trihalomethyl carbanions to give covalent adducts and low yield of the Vicarious Nucleophilic Substitution of Hydrogen (VNS) products. 4,5,6-Trichloropyrimidine in the reactions with carbanions (–CH(X)SO₂Tol, CBr₃) or other nucleophiles (t-BuO⁻, NH₃) gives diverse substituted products of chlorine while in the reaction with CCl₃ anion the VNS product in small amount.
Synthesis of Trioxa[8.3.1] and [13.3.1]-propellanes from 1,1,2,2-Tetrakis(bromomethyl)cyclopropane

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(Received May 17th, 2000; revised manuscript June 16th, 2000)

The synthesis of two new trioxa[8.3.1] 1 and [13.3.1]propellanes 2 is described. Fragmentation path of these compounds on electron impact are discussed as well as their NMR spectra and other physical properties. We have shown that instead of two possibilities ([8.8.1]propellane, [13.13.1]propellane) the general reaction leads to other tri-oxapropellane systems.
Preparation and Properties of 3,1-Benzoxathian-4-one Derivatives

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(Received May 15th, 2000; revised manuscript June 21st, 2000)

A simple preparation of 3,1-benzoxathian-4-one derivatives (3) from thiosalicylic acid and aldehydes, methyl and cyclic ketones, as well as 2,2-dimethoxypropane was developed. The reactivity of 3 under nucleophilic, acidic, reductive and oxidative conditions was examined.
Galanin and Its Analogues Modified in Position 14: Chemical Synthesis and Biological Activity

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(Received May 15th, 2000; revised manuscript June 21st, 2000)

In search of a specific galanin receptor antagonist, 15-amino-acid-residue analogues of porcine galanin modified in position 14 were synthesized and their activity was studied on isolated rat smooth muscles. It was shown that all galanin analogues contracted rat gastric fundus strips in a concentration-dependent manner with significantly increased activities as compared to GAL(1-15)NH₂. The results suggest that position 14 in the amino acid sequence of GAL(1-15)NH₂ is important for the biological activity.
New Approach to Tertiary Carbinamines

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(Received June 5th, 2000; revised manuscript June 21st, 2000)

Tertiary carbinamines (t-alkyl amines) can be conveniently obtained by dephosphorylation of diethyl N-t-alkylphosphoramidates I with 20% hydrochloric acid-tetrahydrofuran (1:1 v/v).
The complexation between the salts of protonated of pyridine, 2-methyl pyridine, 2,4-dimethyl pyridine and 2,4,6-trimethyl pyridine and macrocyclic ligands 18-crown-6, aza-18-crown-6 and 1,10-diaza-18-crown-6 have been studied conductometrically in acetonitrile at different temperature. Formation constants of the resulting 1:1 complexes were determined by the computer fitting of the molar conductance-mole ratio data. The stability of complexes decrease in the sequence: 1,10-diaza-18-crown-6 > aza-18-crown-6 > 18-crown-6. The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constants. In all cases, the complexes were enthalpy stabilized, but entropy destabilized.
Mechanism of Adsorption of Selected Monovalent and Divalent Inorganic Ions at the Alumina/Electrolyte Interface

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(Received December 30th, 1999; revised manuscript June 5th, 2000)

The mechanism of adsorption of selected mono- and divalent ions (Na⁺, Ca²⁺, Cl⁻, SO₄²⁻) at the metal oxide (Al₂O₃)/electrolyte interface has been studied using different experimental techniques: potentiometric titration, zeta potential and adsorption density measurements. Radiotracers and ion-selective electrodes were used to measure the adsorption densities of ions. It was found that the accuracy of both methods was almost the same. Ion-selective electrodes allowed to acquire adsorption data for shorter times of contact between the oxide and electrolyte solution. Based on the potentiometric titration data, ionization and complexation constants of surface hydroxyl groups were calculated using the site binding theory of the electrical interfacial layer. The adsorption density of Ca²⁺, at the same pH and ion concentration, was significantly higher than that observed for sodium ions and revealed strong pH dependence (adsorption edge). A shift of the pzc and iep of alumina was observed in the systems containing chloride, sulphate or calcium ions, due to the specific adsorption of those ions at the oxide/electrolyte interface. The calculated pKₐ values for different anions showed that the stability of surface complexes increased in the following sequence: ClO₄⁻ < Cl⁻ < SO₄²⁻.
Kinetics and Mechanism of Outer-Sphere Reduction of the Oxo-Bridged Trinuclear $\text{[(NH}_3\text{)}_5\text{RuORu(NH}_3\text{)}_4\text{ORu(NH}_3\text{)}_5\text{]}^{7+}$ with Thiosulphate in Acidic Medium

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(Received March 29th, 2000; revised manuscript June 19th, 2000)

The kinetics of the reduction of $\mu$-oxo bridged ruthenium(III,IV) complex, $\text{[(NH}_3\text{)}_5\text{RuORu(NH}_3\text{)}_4\text{ORu(NH}_3\text{)}_5\text{]}^{7+}$, with thiosulphate ion in acidic medium has been investigated by conventional and stopped-flow spectrophotometry in the broad range of reagents concentration, pH and temperature. The reaction follows first order kinetics with respect to the ruthenium complex concentration. The reaction order with respect to $\text{[SO}_2\text{S}^{2-}]$ depends on the reductor concentration and changes from 1 to 2 with $\text{[SO}_2\text{S}^{2-}]$ increase. At a sufficient excess of thiosulphate concentration over the ruthenium complex concentration, the reaction displays saturation kinetics, what can be interpreted by ion-pairs formation between the highly and oppositely charged reactants, followed by one-electron transfer from $\text{SO}_2\text{S}^{2-}$ to the ruthenium centers. The presence of the precursor outer-sphere complexes has been detected kinetically and the rate constants for intramolecular electron transfer within the ion-pairs have been calculated.
Hydrodechlorination of 1,1-Dichlorotetrafluoroethane over Pd/Al₂O₃ Catalyst. Effect of Hydrogen Pressure and Catalyst Pretreatment

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(Received May 5th, 2000; revised manuscript June 20th, 2000)

An alumina-supported palladium catalyst has been studied in CF₃CFCl₂ hydrodechlorination at 100°C using a static-circulation system. At higher partial pressures of H₂, when the existence of the β-PdH phase is awaited, the reaction occurs similarly as at lower hydrogen pressures. This indicates that either the β-PdH formation does not have any special effect on active sites of this reaction, or the presence of CF₃CFCl₂ in the system inhibits this phase transformation. Various pretreatments of the 2 wt.% Pd/Al₂O₃ influence markedly its catalytic behavior. In particular, reoxidation and subsequent low temperature reduction of the catalyst, prereduced at 600°C, generates a very high activity, however, the selectivity towards CF₃CFH₂ is not much altered.
Carbon-13 Kinetic Isotope Effect for the Decarbonylation of Liquid Formic Acid Assisted with Uranium Trioxide, Uranium Peroxide and Uranyl Formate

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(Received March 24th, 2000; revised manuscript June 26th, 2000)

13C KIE’s in the decarbonylation of liquid formic acid (FA) in the presence of uranium trioxide, UO₃, uranium peroxide, UO₂, and in the presence of uranyl formate, UO₂(HCOO)₂, produced in the reaction of the above two uranium oxides with FA have been investigated between 90–120°C. Decarbonylation of HCOOH assisted with uranium trioxide proceeds with normal 13C KIE, expected assuming that 13C–16O bond is broken in the transition state, (k₁₂/k₁₃) KIE = 1.0496 at 100°C. The decarbonylation of liquid formic acid in the presence of uranium peroxide and uranyl formate is accompanied with 13C KIE of intermediate value, which is higher than the 13C KIE observed in the decarbonylation of pure FA, but smaller than the maximum 13C KIE expected for complete rupture of the single carbon–oxygen bond in the decarbonylation T.S. of the protonated formic acid. A mechanism of decomposition of formic acid in the presence of uranium oxides is proposed.
Carbon-13 Kinetic Isotope Effect in the Oxidation of Liquid Formic Acid with Uranium Peroxide

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(Received April 3rd, 2000; revised manuscript June 26th, 2000)

Carbon-13 kinetic isotope effects in the oxidation of liquid formic acid (FA) with uranium peroxide, UO₄, have been studied between 20–120°C. The δ¹³C KIE’s, laying in the range 1.016–1.026, indicate that the full splitting of the δ¹³C–¹H bond takes place in the transition state of this oxidation process. The calculations considering one C–H coordinate only reproduce well the experimental δ¹³C KIE values. At room temperature the experimental δ¹³C KIE = 1.0266 is slightly higher than the calculated 1.0221/20°C, obtained considering only one stretching vibration δ¹³C–¹H, but it is quite close to the δ¹³C KIE observed in the enzymic decarboxylation of FA equal 1.0260. The mechanism of reaction of liquid FA with UO₄ has been proposed.
UV-Visible Absorption Spectroscopic Studies of Intramolecular Proton Transfer in N-(R-Salicylidene)-alkylamines

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(Received January 31st, 2000; revised manuscript June 29th, 2000)

Results of UV-visible spectroscopic studies on thermodynamic parameters of the intramolecular proton transfer equilibrium in N-(R-salicylidene)-alkylamines in solution are presented. The estimated $\Delta H_{TP}$ values in CH$_2$Cl$_2$ solution are within the range $-5.2$ to $-13.9$ kJ/mol. $\Delta S_{TP}$ values are negative: from $-28$ to $-48$ J/molK. The obtained results demonstrate the influence of the acidity of the phenolic group as well as charge delocalization on the position of the proton transfer equilibrium.
Distribution of Trace Amounts of M$^{2+}$ Ions During Crystallization of NiSO$_4$$\cdot$7H$_2$O

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(Received November 19th, 1999; revised manuscript June 30th, 2000)

Distribution coefficients, D, of trace amounts of M$^{2+}$ ions (Fe$^{2+}$, Mg$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, and Mn$^{2+}$) have been determined during isothermal crystallization of NiSO$_4$$\cdot$7H$_2$O at 25$^\circ$C. Their dependencies on the ionic radii of M$^{2+}$ ions, solubilities and structures of the corresponding sulfates as well as their ability to form solid solutions with NiSO$_4$$\cdot$7H$_2$O have been analyzed. The main factors influencing the D values are: the ionic radius of M$^{2+}$ ions and the similarity of structures: MSO$_4$$\cdot$nH$_2$O and NiSO$_4$$\cdot$7H$_2$O as well as their ability to form solid solutions with NiSO$_4$$\cdot$7H$_2$O. The dependence of distribution coefficients on solubility of sulfates in water is disturbed by other factors.
Differential Scanning Hygrometry (DSH) of Some Water Active Inorganic Compounds

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(Received May 9th, 2000; revised manuscript July 3rd, 2000)

Supply of an air flow with a continuously changing water activity from dry air (a_w = 0) up to saturated vapour (a_w = 1) has been applied for acting on powdered water active inorganic compounds placed on the sample panel of a DSC set kept at constant temperature. The absorption of water by the inorganic compounds was monitored by a scanning curve, similar to temperature or pressure induced phase transitions. DSH seems both rapid and inexpensive for monitoring the interaction with water vapour. Comparisons with DSC are discussed and the historical background of DSH is described.
Carbon-Based Ruthenium Catalyst for NH$_3$ Synthesis. Effect of Carbon Treatment

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(Received May 29th, 2000; revised manuscript July 6th, 2000)

The effect of the complex carbon treatment (in sequence: preliminary high temperature heating in an inert atmosphere, partial gasification in CO$_2$ and final heating) on its texture and the activity of the resultant Ba-promoted ruthenium catalysts in NH$_3$ synthesis was studied. Both the preliminary and final heating steps lead mainly to the disappearance of small pores, the effect of the latter step being smaller. In contrast, the gasification (34.0%) in CO$_2$ develops the pore structure of the support. The Ba-Ru/C catalysts proved to be very active and stable in NH$_3$ synthesis ($p = 63$ bar, $T = 400^\circ$C, $x_{\text{NH}_3} = 8\%$), especially those supported on the carbons of well developed texture.
Thermal Reactions of Some Calcium, Strontium and Barium Chromates

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(Received October 14th, 1999; revised manuscript July 10th, 2000)

Thermal decomposition of calcium chromates and solid state reactions of barium and strontium chromates(VI) with barium and strontium hydroxides and carbonates, as well as the reduction of chromates by carbon and hydrogen, have been investigated. The mechanisms of individual stages of the thermal decomposition have been proposed on the basis of the morphological classification.
X-ray Structure of 10-Membered E-Azoxy crown Compound

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Isoelectric Point of Si₃N₄ Measured by an Atomic Force Microscopy

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