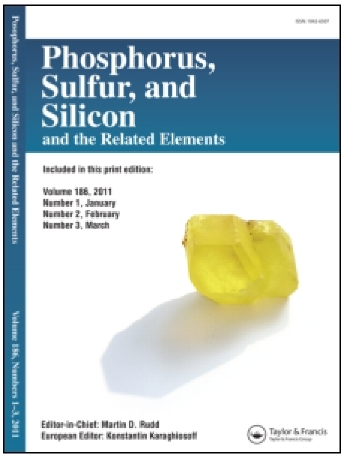

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Aspects Regarding the Synthesis Mechanism and Kinetics of Some Co-Ordination Polymers

IOAN ROŞCA[a], IULIAN RUSU[a]*, ADRIAN CĂILEAN[a],
DANIEL SUTIMAN[a], DOINA SIBIESCU[a], MIHAELA VIZITIU[a] and
MARTIN JOHN SMITH[b]

[a]*Technical University "Gh. Asachi", Faculty of Industrial Chemistry, Department of Inorganic Chemistry, Bd. D. Mangeron 71, 6600 Iaşi, Romania and*
[b]*University of Leeds, School of Chemistry, LS2 9JT, Leeds, England*

The paper presents some aspects regarding the kinetics and mechanisms of the reactions between the Fe(III) and Cr(III) acetylacetonates with phosphinic acids. The experimental data indicate that the mechanism of the studied reactions is an SN2.

Keywords: stabilising energy; yield; rate constant

1. INTRODUCTION

Although the polycoordination process is largely used to obtain polymers, which contain in the main chain coordinated metallic atoms, its kinetics is less studied [1-3]. In order to elucidate some aspects regarding the kinetics and the synthesis mechanism for some coordination compounds we will present experimentally determined data on the interaction of Fe(III) and Cr(III) acetylacetonates with each

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* Corresponding author.

of the following acids: diphenylphosphinic, diphenyltiophosphinic and diphenylditiophosphinic.

2. EXPERIMENTAL

Three series of syntheses, corresponding to the molar reactant ratio of 1:1, 1:2 and 1:3, were performed in organic solvents (ethanol, benzene and toluene). The initial concentrations of the reagents were of 0.1, 0.2 and 0.3 moles/l. The reaction products have the following formulas:

$M_2Acac_4[PO_2(C_6H_5)_2]_2$ denoted as Fe-I and Cr-I
$\{MAcac[PO_2(C_6H_5)_2]_2\}_n$ denoted as Fe-II and Cr-II
$\{M[PO_2(C_6H_5)_2]_3\}_n$ denoted as Fe-III and Cr-III
$\{M[POS(C_6H_5)_2]_3\}_n$ denoted as Fe-IV and Cr-IV
$\{M[PS_2(C_6H_5)_2]_3\}_n$ denoted as Fe-V and Cr-V

The samples collected during the synthesis, from the reaction flask, at different time periods and temperatures were cooled down in order to stop the reaction progress. In order to dose the unreacted reagents, the samples were treated with $NaOH_{(aq)}$ solving the diphenylphosphinic acid and its tio- derivatives. The unreacted acetylacetonates remained in the organic solvents. The amounts of polymer that did not precipitated during the cooling are separated from the organic solvent by dry evaporation. The residue is treated with ether, in which the acetylacetonates are soluble and the polymer is not. The unreacted acetylacetonates and phosphinic acids were determined quantitatively according to literature [4].

3. RESULTS AND DISCUSSION

Plotting the values of the acetylacetonates concentration against time a good linearity was obtained in all cases. This indicates that the partial reaction orders with respect to the acetylacetonates are equal with one. The graphs log [organophosphinic acid]/[acetylacetonate] vs. time, also presented a good linearity, meaning that the total reaction orders are equal with two. The activation energies were determined according to the Arhenius equation, plotting the values of log k (where k is the rate constant) as a function of 1/T (where T is the absolute temperature) and extracting the values from the slopes of the graphs. The obtained results are listed in Table 1.

Compound	Fe-I	Fe-II	Fe-III	Fe-IV	Fe-V
$k\cdot10^{-3}$ ($l\cdot mole^{-1}\cdot s^{-1}$)	5.1	3.8	2.7	0.83	0.92
E_a ($kJ\cdot mole^{-1}$)	78.2	89.8	106.6	75.8	65.2

Compound	Cr-I	Cr-II	Cr-III	Cr-IV	Cr-V
$k\cdot10^{-3}$ ($l\cdot mole^{-1}\cdot s^{-1}$)	4.8	33.1	1.1	6.9	7.9
E_a ($kJ\cdot mole^{-1}$)	90.7	99.0	111.6	81.8	72.5

TABLE I. Values of rate constants at 80°C and of the activation energy for the synthesis reactions of the studied compounds

As can be observed from the table, the activation energies depend on the nature of both the central atom and the ligand. However, the consecutive differences between the activation energies in the same series (e.g. iron series or chromium series) are larger than the differences between the activation energies for the compounds having the same ligand (e.g. Fe-I and Cr-I). This means that the polycoordination process is much stronger influenced by the ligand's nature than the central ion. On the other hand, the activation energies are higher for the chromium compounds comparing with those of the similar iron products. When the coordination is achieved by means of sulphur atoms, the activation energies are much lower than those corresponding to the coordination by means of oxygen atoms. This behaviour could be explained taking into account that, due to its lower electronegativity, the sulphur is more distortable, polarizing and polarizable than the oxygen, favouring the engaging of the outer electrons on coordination bonds with the free orbitals of central ions.

The reaction mechanism could be understood in terms of substitution between ligands (the acetylacetonate ligands are substituted by the diorganophosphinic anions) [11]:

- By the lowering of the coordination number of the central ion with a unit, due to the detaching of a ligand. This is a slow process, followed by a quick coordination of the substituting ligand. The entire reaction is a first order nucleophile substitution (SN1).
- By the increase of the coordination number with one unit, due to the coordination of the substituting ligand at the central ion, followed

by a quick elimination process of the substituted ligand. The reaction is a second order nucleophile substitution (SN2).

We will exemplify the mechanism for the compounds Fe-I and Cr-I, the other's behaviour being similar with this one. The chemical analysis indicates that for each central ion correspond three bidentate ligands: one from the Acac⁻ anion and two from the diphenylphosphinic acid. Therefore, the central ion has an octahedral configuration. The calculated stabilising energy in crystalline field (SECF) [5] of the octahedral configuration for the Fe(III) ion is of 20 Dq. If we consider and SN1 mechanism, the coordination number is decreasing to five and we have to admit a trigonal bipyramidal structure for the activated complex. In such a situation, the calculated SECF value of the activated complex is of 19.14 Dq and corresponds to a lowering of its value with 0.86 Dq comparing with the octahedral structure. The SN2 mechanism can be proposed only if the central ion has free d orbitals. Both Fe(III) and Cr(III) ions have such free orbitals. However, in this case the coordination number of the activated complex will be seven. Despite the fact that is not the only possible structure, the literature indicates a pentagonal bipyramidal configuration [1]. The addition of the diphenylphosphinic acid at the central ion could be achieved on one of the octahedral faces. The second step is quick and implies the detaching of an Acac⁻ ion from two activated complexes and the recovery of the initial coordination number by the bidentate coordination of the diphenylphosphinic anion at the two central ions. If we repeat the above calculations with the Fe(III) ion, the SECF for the pentagonal bipyramidal configuration is of 18.3 Dq, being lower with 1.7 Dq than the octahedral structure. Therefore, these results lead to the conclusion that the most appropriate mechanism is SN2. Performing the same analysis for the chromium complex we have arrived at the same conclusion.

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