Research Article

Catalytic Potential of Mononuclear Cr(III)-Imine Complexes for Selective Oxidation of Benzyl Alcohol by Aqueous H_2O_2

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Abstract Chromium(III) complexes were derived, as tri- and tetradentate imine chelates, from 2-hydroxy-1-napthaldehyde or 3-ethoxysalicylaldehyde with 2-aminophenol or 1,2-phenylenediamine. The catalytic potentials of Cr(III)-imine chelates were probed and tested in the chemoselective benzyl alcohol oxidation to benzaldehyde (BA) within an eco-friendly terminal oxidant (i.e., H_2O_2). The effect of various applicable parameters in the catalytic systems (e.g., solvents, temperature, and catalyst molar ratios) was studied. From the obtained results, it is found that the most favored and suitable solvent applied is acetonitrile at best reaction conditions; temperature $80\,°C$ after 4 h. The mechanistic aspects of the Cr(III)-catalyzed oxidation were tentatively described and discussed based on electron and oxygen transfer processes.

Keywords chromium(III); imines; benzyl alcohol; catalytic oxidation; selectivity; hydrogen peroxide

1. Introduction

Catalytic alcohol oxidation to corresponding carbonyl compounds, such as aldehydes or ketones, is a main subject of the synthetic strategy in organic chemistry [1,2]. Fragrances and food additives as well as fine organic chemicals are an essential necessity for alcohols oxidation [3].

Benzaldehyde (BA), as one of the most required carbonyl compounds in marketing, is the chemo-, sterio-, and regioselective product of benzyl alcohol oxidation protocols catalytically [4]. Many transition metal complexes were initiated for such catalytic processes as homogeneous catalysts [5,6,7] to improve the yield percentages of the chemoselective products aldehydes or ketones and to avoid the most competitive oxidation products as the corresponded carboxylic acids [8,9]. As for the development of new models of metal-complexes catalysts, as valuable and effective catalysts for the alcohols oxidation, Cr(VI)-imine complexes are counted as the first attempt to use chromium ions in its complexes as homogeneous catalysts [10]. Variation of chromium ion concentration, its ability to adopt multiple oxidation states from $+2$ to $+6$ positive charge [11] as well as its cheap cost motivated us to involve some Cr(III)-imine chelates as homogenous catalysts for the benzyl alcohol oxidation with the highest welcomed effective and environmental oxidant H_2O_2 [12].

Transition metal complexes with imine ligands as Schiff base derivatives [13] are cataloged as the backbone of the catalysts for the oxidation of alcohols, thioles, thiophenes, and olefins due to their commercially cheap, easy preparation and specific chemical and thermal stability in both solid and liquid phases [14,15,16]. In addition, another component of our catalytic system is the oxidant, that is, H_2O_2, which is widely used and applied for being a clean and inexpensive oxidant.

Thus, we present here the catalytic studies of Cr(III)-imine complexes as homogeneous catalysts for benzyl alcohol oxidation. The catalytic potentials of the current Cr(III)-imine chelates were studied with various effective parameters, for example, different solvents, time, temperature, and oxidant in aerobic oxidation of benzyl alcohol. A proposed mechanism for the catalytic processes was suggested depending upon the spectroscopic characteristics.

2. Experimental

2.1. Reagents and methodologies

Reagents utilized for synthetic and catalytic processes are available from Merck, Fluka, and Aldrich. All of them were used without further purification. IR spectra were studied using Shimadzu FTIR-8300 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were achieved in Bruker Avance DPX-500 spectrometer. UV-V is spectral scans were assigned using 10 mm matched quartz cells through PG spectrophotometer model T+80. Elemental analyses were carried at the main lab of Cairo University by elemental analyzer (Perkin-Elmer, model 240c). The magnetic instrument was used to record the magnetic features of Cr(III)-complexes by using Gouy's balance. Molar conductivity properties were

Table 1: Analytical and physical characterization data of H_2LA1 and CrLA1.

Comp.	M. wt.	Color yield (%)	Λ_m (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (B.M.)	m.p. (°C)	Analysis (%) (found (calc.))		
						C	H	N
H_2LA1	$C_{17}H_{13}NO_2$ (263.09)	Yellow	—	—	140	77.41 (77.52)	4.91 (4.98)	5.28 (5.32)
CrLA1	$C_{17}H_{19}N_2O_9Cr$ (477)	Deep brown	7.02	4.08	220	45.53 (45.64)	4.28 (4.25)	6.31 (6.26)

Table 2: Characteristic IR bands of the prepared imine ligand and its complexes.

Compound	$v_{(OH)/H_2O}$	$v_{(CH)ar}$	$v_{(C=N)}$	$v_{(C-O)ph}$	$v_{(Cr-O)}$	$v_{(Cr-N)}$
H_2LA1	3,448	3,120	1,634	1,240	—	—
CrLA1	3,378	3,321	1,623	1,212	567	460

Table 3: Thermal decomposition steps, mass loss (%), proposed lost segments, final residue thermo-kinetic activation parameters of each decomposition step for the prepared complexes.

Comp.	Decomp. temp. (°C)	Mass loss (%) Found	Calc.	Proposed segment	E^* (KJmol^{-1})	$A(S^{-1})$	ΔH^* (KJmol^{-1})	ΔG^* (KJmol^{-1})	ΔS^* (Jmol^{-1}K^{-1})
CrLA1	35–110	8.12	8.05	$2H_2O$	78.3	0.096	77.8	93.6	−251.55
	112–211	8.22	8.05	$2H_2O$			78.3	119.7	−259.52
	213–285	13.78	13.87	NO_3			76	141.7	−262.97
	287–399	31.65	31.77	$C_{10}H_6O$			75.5	165.8	−265.5
	401–567	26.52	26.60	C_7H_5NO			74.2	205.8	−268.57
Residue	> 567	11.70	11.63	Cr			—	—	—

performed by using conductivity meter model JENWAY 4510. Thermogravimetric analysis was made under nitrogen with a heating rate $10\,°C\,min^{-1}$ on Shimaduz corporation 60H analyzer. The absorbance of the compounds was determined at a concentration of 5×10^{-3} M at 25 °C.

2.2. Preparation of imine ligands (H_2LA1, H_2LA2, and H_2LA3)

H_2LA1 ligand was prepared through the condensation of an ethanolic 2-hydroxy-1-napthaldehyde (5.0 mmol) with 2-aminophenol (5.0 mmol). The obtained reaction mixture was refluxed for 1 h at 80 °C. The accomplishment of the synthetic route was followed by TLC. The solvent was evacuated affording very concentrated solution and then left to cool. Yellow crystals of H_2LA1 were observed, then filtered out. The precipitate was washed with cold ethanol and dried in a desiccator. The ligand was characterized by alternative physico-chemical tools and reported in Tables 1, 2, and 3.

H_2LA2 ligand was synthesized as reported previously by mixing of 3-ethoxsalicyaldehyde (5.0 mmol) in ethanol with an ethanolic media of 2-aminophenol (5.0 mmol) [17].

H_2LA3 ligand was synthesized also as reported previously by common condensation of an ethanolic 2-hydroxy-1-napthaldehyde (10 mmol) with o-phenelendiamine (5.0 mmol) [18].

NMR data of H_2LA1

^{1}H-NMR (DMSO-d_6, 400.1 MHz): $\delta = 6.83$ (d, $^3J = 6.8$ Hz, 1H, H-3′), 6.95 (dd, $^4J = 1.1$, $^3J = 5.8$ Hz, 1H, H-5′), 7.03 (d, $^3J = 7.1$ Hz, 1H, H-6′), 7.12 (dt, $^4J = 0.9$, $^3J = 6.5$, 7.0 Hz, 1H, H-4′), 7.27 (s, 1H, H-3), 7.49 (dd, $^3J = 5.9$, 6.2 Hz, 1H, H-6), 7.68 (dt, $^4J = 2.0$, $^3J = 6.0$, 6.3 Hz, 1H, H-7), 7.79 (d, $^3J = 6.0$ Hz, 1H, H-8), 7.86 (dd, 1H, $^4J = 1.8$, $^3J = 5.8$, 6.1 Hz, H-5), 8.36 (d, 1H, $^3J = 6.2$ Hz, H-4), 9.49 (s, 1H, CH=N), 10.15 (s, 1H, phenyl-OH) and 15.65 ppm (s, 1H, naphthyl-OH).

^{13}C-NMR (DMSO-d_6, 100.6 MHz): $\delta = 108.3$ (C$_q$), 116.6 (CH), 118.3 (CH), 120.2 (d, J = Hz, CH), 123.4 (CH), 125.2 (CH), 126.4 (C$_q$), 127.1 (CH), 128.5 (CH), 129.4 (CH), 129.6 (C$_q$), 134.3 (C$_q$), 138.1 (C$_q$), 149.1 (C$_q$), 150.4 (CH) and 177.1 ppm (CH=N).

NMR spectral data of H_2LA2 and H_2LA3 are reported [17, 18].

2.3. Preparation of Cr(III)-complexes (CrLA1, CrLA2, and CrLA3)

Cr(III)-imine complex (CrLA1) was prepared by mixing of 5.0 mmol of H_2LA1 in ethanol with 5.0 mmol of chromium nitrate hexahydrate in water. The mixed solution was refluxed for 2 h at 85 °C. The solvent was evaporated and the resulted precipitate was washed with ethanol and desiccated over anhydrous $CaCl_2$. The novel complex (CrLA1) was characterized by alternative physico-chemical tools and reported in Tables 1, 2, and 3.

CrLA2 and CrLA3 were prepared with a reported procedure [17, 18]: 5.0 mmol of H_2LA2 or H_2LA3 in ethanol was reacted with 5.0 mmol of $Cr(NO_3)_3 \cdot 6H_2O$ in water.

2.4. Stoichiometry evaluation and apparent formation constants

The molar ratio [14, 15, 16] and continuous variation methods [19] were applied to determine the equilibria in its solutions and to evaluate the ratio of metal ion to the coordinated ligands, as M : L ratio.

Formation constant values (K_f) of Cr(III)-imine complexes, which are investigated in solutions, are derived from the spectrophotometric measurements with operating of the continuous variation method [14, 15, 16] as follows:

$$K_f = \frac{A/A_m}{(1 - A/A_m)^2 C}, \tag{1}$$

where A_m is the maximum formation absorbance value of the studied coordination compound and A is the alternative absorbance depending on the initial concentration of Cr^{3+} ions (C). Free energy change value of CrLA1, $\Delta(G^*)$, could be derived for the equation; $\Delta(G^*) = -RT \ln K_f$ at room temperature, where K_f is representative of the formation constant and R is the gas constant. Formation constant value of CrLA1 is listed in Table 3, whereas those values of CrLA2 and CrLA3 are recorded previously [17, 18].

2.5. Kinetic studies

Coast-Redfern integral method was used to derive the kinetic parameters of decomposition analysis of Cr(III)-imine complexes [20, 21]. The thermogravimetric decomposition analysis was presented step by step in Table 3 for CrLA1. The thermodynamic parameters, the energy of activation (E^*), the entropy of activation (ΔS^*), enthalpy (ΔH^*), and free energy change (ΔG^*) of the CrLA2 and CrLA3 decomposition were reported elsewhere [17, 18]. Those values for CrLA1 were obtained by using

$$\log \left[\frac{\log \left(\frac{w_\infty}{w_\infty - w} \right)}{T^2} \right]$$
$$= \log \left[\frac{AR}{\phi E^*} \left(1 - \frac{2RT}{E^*} \right) - \frac{E^*}{2.303RT} \right], \tag{2}$$

where w_∞ is represented as the mass loss at the end of thermal run, w is represented as the mass loss detente, T is for temperature, R is already defined as the gas constant, and the heating rate is defined as ϕ. The relationship $1 - 2RT/E^*$ equal to 1, approximately, plotting of that relationship of (1) versus $1/T$ could calculate E^* from the slope and A derived from the intercept. In equations (3)–(5), the kinetic parameters ΔS^*, ΔH^*, and ΔG^*, entropy and enthalpy of activation, and the free energy change of activation, respectively, could be calculated [20, 21]:

$$\Delta S^* = 2.303 R \log \frac{Ah}{K_B T}, \tag{3}$$
$$\Delta H^* = E^* - RT, \tag{4}$$
$$\Delta G^* = H^* - T \Delta S^*, \tag{5}$$

where K_B and h are Boltzmann's and Plank's constants, respectively. For CrLA1, the kinetic parameters are presented in Table 3, but the kinetic parameters of CrLA2 and CrLA3 are presented in previous works [17, 18].

2.6. Catalytic procedures

Benzyl alcohol as a standard substrate (0.13 mL, 1.0 mmol) in 10 mL of acetonitrile (or other solvents) was added to 0.02 mmol of Cr(III)-chelate catalysts (CrLA1, CrLA2 or CrLA3) contacted with air under aerobic conditions at 60 °C, 70 °C, 80 °C, 90 °C or 100 °C in an oil bath with continuous stirring. The catalytic process was motivated by being charged with 0.1 mL aqueous H_2O_2 (30%, 3.0 mmol) at the applied reaction temperature. The process progressing was followed by GC investigated by the standard calibration curve. The chemoselective product was determined by the comparison of its time of retention with that of the authentic sample. The catalytic reactions were followed to determine the optimal conditions by withdrawing samples (1.0 mL) from the reaction media and treated by potassium thiosulfate to destroy the excess H_2O_2 and to absorb water in each catalytic experiment. The obtained slurry was filtered on celite, and the filtrate was diluted by acetonitrile and injected to GC instrument. The percentage of selective conversion of benzyl alcohol to BA was calculated by the standard calibration curves [22]. Agelient 5890A 19091J-413: 325 °C as GC is computerized and attached with FID (flame ionization detector) and an HP-5 capillary column (phenyl methyl siloxan 30 m × 320 μm × 0.25 μm). The temperature of injection was 250 °C. The initial temperature was 140 °C for 1 min, and then increased 10 °C per min to 250 °C, and held for 1 min at this temperature. Helium is the carrier gas. The common known products, BA and benzoic acid (BZ), were identified by a comparison of their retention times with their reference compounds. Each catalytic experiment was run in duplicate. The internal standard method was applied to quantify the reaction product.

3. Results and discussion

3.1. Cr(III)-complexes characterization

The full characterization of H_2LA2 and H_2LA3 are reported elsewhere [17, 18], whereas H_2LA1 and its corresponding Cr-complex (CrLA1) are studied and discussed here in this work.

Cr(III)-imine complexes (CrLA1, CrLA2, and CrLA3) are tinted in solid phase at 25 °C and nonhygroscopic in nature. The elemental analysis results of H_2LA2, H_2LA3, and their Cr(III)-complexes are presented elsewhere [17, 18]. The elemental analysis results of CrLA1 and its coordinated ligand H_2LA1 are listed in Table 1, which are convenient with the theoretical percentages of CHN elements. Consequently, H_2LA1 behaved as coordinated chelating agent towards Cr(III) ion as tri-dentate in 1 : 1 ratios to
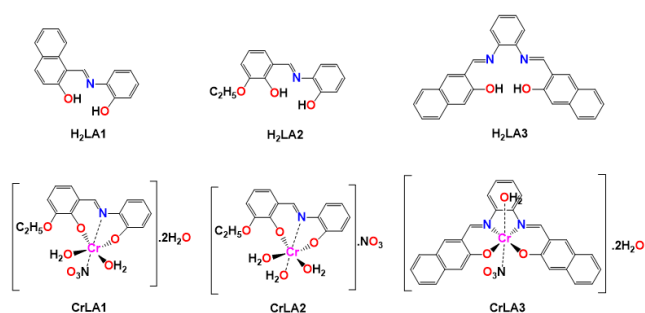
Scheme 1: Molecular structure of H$_2$LA1, H$_2$LA2, and H$_2$LA3 ligands, and their Cr(III)-complexes (CrLA1, CrLA2, and CrLA3).

Cr^{3+} ion in an octahedral geometry, similar to CrLA2. The molar conductance of CrLA1 was measured at 25 °C in DMF with 7.02 Ω^{-1} cm^2 mol^{-1}, as summarized in Table 1. The conductivity value implies the nonelectrolytic nature of CrLA1 and is convenient with the suggestion that the NO$_3^-$ anion is in the coordination sphere (Scheme 1). Magnetic moment measurements of CrLA2 and CrLA3 are recoded elsewhere [17, 18], affording paramagnetic properties, but for CrLA1, it is reported in Table 1. The paramagnetic feature of CrLA1 is recorded with magnitude 4.08 BM.

3.1.1. ^{1}H-NMR and ^{13}C-NMR spectra of H$_2$LA1

^{1}H- and ^{13}C-NMR spectra of H$_2$LA2 and H$_2$LA3 are already presented previously [17, 18]. The ^{1}H- and ^{13}C-NMR spectral scans and their data of H$_2$LA1 are listed in Section 2. The most characteristic ^{1}H-NMR spectrum of H$_2$LA1 showed a singlet signal at 15.65 of naphthyl-OH, at 10.15 of phenyl-OH, and 9.49 ppm of azomethine group (CH=N). The rest signals belong to the aromatic protons of phenyl and naphthyl rings in H$_2$LA1.

The most distinguished ^{13}C-NMR signal is at 177.1 ppm as CH signal of H$_2$LA1, which is assigned to azomethine carbon. The other signals, detected in the region 150.4-10.3 ppm, are exhibited for the phenyl and naphthyl carbon atoms.

3.1.2. Infrared spectra

The featured IR wave number data of the H$_2$LA2, H$_2$LA3, and their complexes (CrLA2 and CrLA3) are reported [17, 18]. For H$_2$LA1 and CrLA1, the most significant vibrational bands are tabulated in Table 2. The −OH and −CH=N− groups are assigned with broad and sharp bands in H$_2$LA1 at 3,448 cm^{-1} and 1,634 cm^{-1}, respectively. With complex formation with Cr^{3+} ion, the −OH band could not be observed anymore and the −CH=N− band was notably low shifted to 1,583 cm^{-1}. That lower shifting after CrLA1 formation of the azomethine nitrogen atoms could prove the role of nitrogen lone pair of azomethine group to bond to Cr^{3+} ion within coordinated bond [23]. An additional
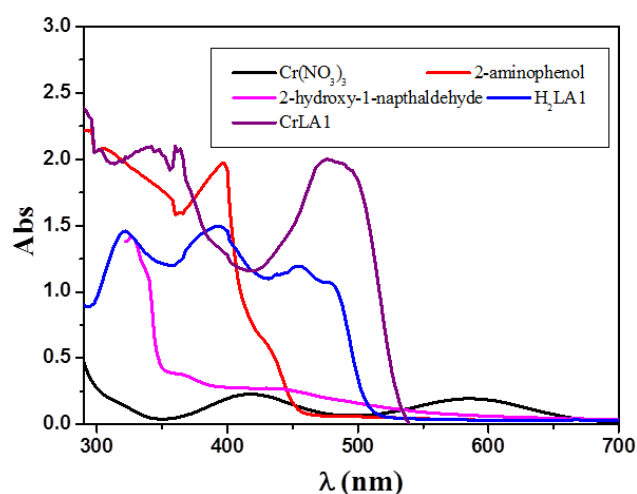

Figure 1: The electronic spectra of reagents and their synthesized H$_2$LA1 and its corresponded complex (CrLA1).

band was detected at 3,378 cm^{-1} due to the appearance of the coordinated water molecules or the crystalline molecules. This suggestion could be supported by the presence of new stretching weak bands at 567 cm^{-1} and 460 cm^{-1}, corresponding to the Cr−O and Cr−N bonding formation (Table 1) [23, 24]. The distinguished frequencies of NO$_3^-$ group in CrLA1 have three nondegenerated modes at 1,470 cm^{-1} $v_{(NO_2)asy}$, 1,356 cm^{-1} $v_{(NO_2)sy}$, and 851 cm^{-1} $v_{(NO)}$ [25].

3.1.3. UV-Vis spectra

The molecular electronic transition spectral measurements of H$_2$LA2, H$_2$LA3, CrLA2, and CrLA3 were recorded and discussed before [17, 18]. Here we presented only the characteristic electronic absorption transitions of H$_2$LA1 and its Cr-complex (CrLA1) to utilize their stereochemistry according to the sites and number of possible electronic transition bands [16]. H$_2$LA1 shows two registered bands at 355 nm and 496 nm for the $n \to \pi^*$ and L-CT transitions in the visible regions [22, 26]. CrLA1 assigned three bands at 338 nm, 404 nm, and 450 nm, which are resulted from $n \to \pi^*$ and ML-CT, and d−d transitions. The band d−d could be mainly proven by the formed Cr-complex (Figure 1).

3.1.4. Thermal analysis

The thermal behavior of CrLA2 and CrLA3 was presented previously [17, 18]. But CrLA1 was analyzed thermally and the results were illustrated in Table 3. In the table, the hydrated CrLA1 in the crystal lattice lost two H$_2$O molecules in the first step. That mass loss was 8.12%, which agrees with the calculated values 8.05%. The second loss is the two H$_2$O coordinated molecules with decomposing of the coordinated ligand molecule in the next steps, as noted in Table 3. The experimental percentage loss is 8.22%,

which is also convenient with the theoretical one, 8.05%. The TGA curve of CrLA1 shows loss in weight within the temperature range 213–285 °C, which is attributed to the removal of the coordinated nitrate anion (found 13.87% and calc. 13.78%). Furthermore, CrLA1 assigned mass loss in the temperature range 287–399 °C, which is resulted from the loss of an organic part of the coordinated ligand ($C_8H_8O_2$) with mass losses (found 31.65% and calc. 31.77%). The last decomposition step was done for the organic species at the range of temperature 401–567 °C with mass losses (found 26.52%, calc. 26.60%), leading to the loss of the last species of the coordinated ligand. At the end, formation of free Cr atoms as the final product was discovered at temperature more than 567 °C (found 11.70%, calc. 11.63%) [23, 24].

3.1.5. Kinetic aspects

Kinetic parameters are displayed in Table 3. The value of G^* was increased by temperature arising. The H^* was recorded as a positive value referring to endothermic decomposition processes of CrLA1. Moreover, the negative value of S^* suggested a decomposition via abnormal pathway at the above decomposed steps. The negative activation entropy proposes a high order of the formed complex CrLA1 than that of the substrates and so the formation reactions are considered to be slow. Furthermore, the positive values of H^* and G^* (Table 3) suggested endothermic features for each thermal step [23, 24, 27].

3.1.6. Stoichiometry spectrophotometric apparent formation constants determinations

Stoichiometry of CrLA2 and CrLA3 is determined previously [17, 18]. For CrAL1, its stoichiometry was determined within two various methods spectrophotometrically; first is the continuous-variations method and second is the mole-ratio method. The obtained results showed that the stoichiometry of CrLA1 is 1 : 1 [22, 26].

The formation constants (K_f) of CrLA2 and CrLA3 are reported and presented elsewhere [17, 18]. Here K_f value was evaluated only for CrLA1 depending upon the spectrophotometric measures of the continuous variation method. The obtained K_f value displays a high stability of CrLA1. In addition, stability constant (pK) and Gibbs free energy ($\Delta G^{\neq}$) values of CrLA1 were derived and calculated (Table 3). The negative value of Gibb's free energy means that CrLA1 formation reaction of H_2LA1 and Cr^{3+} ion is spontaneous and favored.

3.2. Catalytic activity of Cr(III)-imine complexes

The catalytic reactivity of the three Cr(III)-imine complexes was investigated in the oxidation of benzyl alcohol (R) as a standard model of primary alcohols with an aqueous H_2O_2, as an oxygen donor, to the corresponding carbonyl compound, BA, in various aerobic conditions. A series of blank tests revealed that the presence of Cr^{III}-catalyst and H_2O_2, as the oxidant, is essential for an effective catalytic oxidation of benzyl alcohol (Tables 4, 5, and 6). In order to find the optimized reaction conditions, the effect of alternative reaction parameters was studied that may influence the control chemoselective conversion to BA. Temperature, time, and solvent are the most fundamental factors that have been examined to get the optimized catalytic processes.

So far in literature, catalytic studies on Cr(III) complexes are reported for the oxidation of alcohols or (ep)oxidation of alkenes and alkanes [11, 28]. Some attempts have been published for the investigation of the catalytic potentials of some Cr(III)-complexes supported on silica gel [29] or MCM-41 [30]. It is a new attempt to present here the catalytic activity of new Cr(III) complexes of tri- and tetradentate imine ligands with different moiety and bulkiness.

The benzyl alcohol (R) (1.0 mmol) oxidation processes are carried out with an aqueous H_2O_2 (3.0 mmol) in acetonitrile (10 mL) at various temperatures and for different times catalyzed by CrLA1, CrLA2 or CrLA3 with various catalytic molar ratios of the catalysts (0.02 mmol, 0.05 mmol or 0.10 mmol); as shown in Tables 4, 5, 6, and 7. The obtained oxide products could be analyzed and identified by GC. Controlling of each experiment showed that no oxide product (P) could be formed in the absence of Cr(III)-catalyst.

3.2.1. Effect of temperature and time

The controlled catalytic processes using CrLA1, CrLA2 or CrLA3 catalyst were entirely chemoselective for oxidation. BA, as the major target product, was obtained in the highest scale, but there were other unwelcomed side products in alternative conditions, as obtained by the turnover numbers (TON) and turnover frequencies (TOF) (Tables 4, 5, and 6).

Depending upon temperature control, at 60 °C, the conversion of A to BA catalyzed by CrLA1, CrLA2 or CrLA3 was very low, but the chemoselectivity was an excellent approach to 100% as observed in Tables 4, 5, and 6 (entries 1 and 2) for all catalysts after 4 h. But by time, the selectivity was reduced for all catalyst complexes after 6 h to be 71%, 61%, and 60% with CrLA1, CrLA2, and CrLA3, respectively, see entry 4 in Tables 4, 5, and 6. At 60 °C, the reaction temperature is not enough for improving the catalytic potential of the studied Cr(III)-catalysts.

By increasing of the reaction temperature to 70 °C, the conversion was improved unremarkably in the identical conditions (Tables 4, 5, and 6, entries 5 and 6), and the selectivity was excellent (100%), affording good yield of BA (47%, 44%, and 40% catalyzed by CrLA1, CrLA2, and CrLA3, resp.) after 2 h with no observation of BZ as a further oxidized product. With time running, the percentages of BA were enhanced with time after 4 h to 52%, 49%, and 43% by CrLA1, CrLA2, and CrLA3, respectively, with

Table 4: Oxidation of benzyl alcohol catalyzed by CrLA1 using an aqueous H_2O_2 in acetonitrile.

Entry[a]	Temp (°C)	Time (h)	Yield (%)[b]				Conversion (%)	Selectivity (%)	TON[d]	TOF[e]
			BA[b]	BZ[c]	Side products	R[a]				
1	60	1	29	—	—	71	29	100	14.5	14.5
2		2	33	—	—	67	33	100	16.5	8.2
3		4	38	0	—	62	40	95	19	4.7
4		6	27	13	—	60	38	71	13.5	2.2
5	70	1	42	—	—	58	42	100	21.0	21.0
6		2	47	—	—	53	47	100	23.5	11.7
7		4	52	3	—	45	55	95	26.0	6.5
8		6	46	7	—	47	53	87	23.0	3.8
9	80	1	58	—	—	42	58	100	29.0	29.0
10		2	77	—	—	23	77	100	38.5	19.2
11		4	93	—	—	7	93	100	46.5	11.6
12		6	75	21	—	4	85	88	37.5	6.2
13	90	1	45	23	—	32	68	66	22.5	22.5
14		2	39	27	11	23	77	51	19.5	9.7
15		4	28	32	20	20	80	35	14.0	3.5
16		6	24	36	21	19	81	30	12.0	2.0
17	100	1	32	33	10	25	75	48	16.0	16.0
18		2	25	42	17	16	84	33	12.5	6.2
19		4	19	53	21	8	93	25	9.5	2.4
20		6	15	60	25	2	98	15	7.5	1.2

[a]The oxidation of benzyl alcohol (R) (1.0 mmol) catalyzed by complex CrLA1 (0.02 mmol) with aqueous H_2O_2 (3.00 mL) in 10 mL acetonitrile for 1–6 h.
[b]The yield based on GC results, selectivity percentage of the target oxide product BA and the other product BZ.
[c]The other side products are mainly of BZ.
[d]TON (turnover number) = ratio of moles of product (here oxide) obtained to the moles of catalyst.
[e]The corresponding TOF (turnover frequency) (TON/h) are shown in parentheses (mol (mol catalyst)$^{-1}$ h^{-1}).

Table 5: Oxidation of benzyl alcohol catalyzed by CrLA2 using an aqueous H_2O_2 in acetonitrile.

Entry[a]	Temp (°C)	Time (h)	Yield (%)[b]				Conversion (%)	Selectivity (%)	TON[d]	TOF[e]
			BA[b]	BZ[c]	Side products	R[a]				
1	60	1	25	—	—	75	25	100	12.5	12.5
2		2	29	—	—	71	29	100	14.5	7.25
3		4	34	—	—	66	34	100	17	4.25
4		6	22	14	—	64	36	61	11	1.83
5	70	1	39	—	—	61	39	100	19.5	19.5
6		2	44	—	—	56	44	100	22	11
7		4	49	1	—	50	54	91	24.5	6.13
8		6	41	13	—	46	50	82	20.5	3.42
9	80	1	53	—	—	47	58	100	26.5	26.5
10		2	70	—	—	30	77	100	35	17.5
11		4	85	—	—	15	85	100	42.5	10.63
12		6	69	21	—	10	81	85	34.5	5.75
13	90	1	41	21	—	38	62	66	20.5	20.5
14		2	34	25	9	32	68	51	17	8.5
15		4	25	29	17	29	71	35	12.5	3.13
16		6	22	33	19	26	74	30	11	1.83
17	100	1	29	31	7	33	67	43	14.5	14.5
18		2	21	40	15	24	76	28	10.5	5.25
19		4	16	51	19	14	86	19	8	2
20		6	13	57	23	7	93	14	6.5	1.08

[a]The oxidation of benzyl alcohol (R) (1.0 mmol) catalyzed by complex CrLA2 (0.02 mmol) with aqueous H_2O_2 (3.00 mL) in 10 mL acetonitrile for 1–6 h.
[b]The yield based on GC results, selectivity percentage of the target oxide product BA and the other product BZ.
[c]The other side products are mainly of BZ.
[d]TON (turnover number) = ratio of moles of product (here oxide) obtained to the moles of catalyst.
[e]The corresponding TOF (turnover frequency) (TON/h) are shown in parentheses (mol (mol catalyst)$^{-1}$ h^{-1}).

Table 6: Oxidation of benzyl alcohol catalyzed by CrLA3 using an aqueous H_2O_2 in acetonitrile.

Entry[a]	Temp (°C)	Time (h)	Yield (%)[b]				Conversion (%)	Selectivity (%)	TON[d]	TOF[e]
			BA[b]	BZ[c]	Side products	R[a]				
1	60	1	19	—	—	81	19	100	9.5	9.5
2		2	23	—	—	77	23	100	11.5	5.75
3		4	29	—	—	71	29	100	14.5	3.63
4		6	18	12	—	70	30	60	9	1.5
5	70	1	35	—	—	65	35	100	17.5	17.5
6		2	40	—	–	60	40	100	20	10
7		4	43	2	—	55	45	96	21.5	5.38
8		6	39	7	—	54	46	85	19.5	3.25
9	80	1	46	—	—	54	46	100	23	23
10		2	63	—	—	37	63	100	31.5	15.75
11		4	74	—	—	36	74	100	37	9.25
12		6	60	9	—	31	81	87	30	5
13	90	1	37	19	—	44	56	66	18.5	18.5
14		2	30	22	6	42	58	52	15	7.5
15		4	23	25	14	38	62	37	11.5	2.88
16		6	18	30	16	36	64	28	9	1.5
17	100	1	26	28	5	41	59	44	13	13
18		2	19	37	12	32	68	28	9.5	4.75
19		4	14	48	16	22	78	18	7	1.75
20		6	10	53	19	18	82	12	5	0.83

[a]The oxidation of benzyl alcohol (R) (1.0 mmol) catalyzed by complex CrLA3 (0.02 mmol) with aqueous H_2O_2 (3.00 mL) in 10 mL acetonitrile for 1–6 h.
[b]The yield based on GC results, selectivity percentage of the target oxide product BA and the other product BZ.
[c]The other side products are mainly of BZ.
[d]TON (turnover number) = ratio of moles of product (here oxide) obtained to the moles of catalyst.
[e]The corresponding TOF (turnover frequency) (TON/h) are shown in parentheses (mol (mol catalyst)$^{-1}$ h^{-1}).

Table 7: Effect of solvent on the catalytic activity of benzyl alcohol oxidation by Cr(II) complexes at optimum conditions.

Catalyst	Solvent[a]	Yield (%)				Conversion (%)	Selectivity (%)
		BA[b]	BZ[c]	Side products	R		
CrLA1	CH_2Cl_2	53	3	31	13	87	61
	Acetone	67	6	18	9	91	74
	$CHCl_3$	25	3	84	24	76	33
	DMF	—	—	100	—	100	0
CrLA2	CH_2Cl_2	40	2	39	19	81	49
	Acetone	57	5	23	16	84	68
	$CHCl_3$	24	1	55	20	80	30
	DMF	—	—	96	4	96	0
CrLA3	CH_2Cl_2	36	2	31	31	69	50
	Acetone	51	4	17	28	72	71
	$CHCl_3$	15	3	48	34	66	23
	DMF	—	—	89	11	89	0

[a]The oxidation of benzyl alcohol (R) (1.0 mmol) catalyzed by complex CrLA2 (0.02 mmol) with aqueous H_2O_2 (3.00 mL) in 10 mL acetonitrile for 1–6 h.
[b]The yield based on GC results, selectivity percentage of the target oxide product BA and the other product BZ.
[c]The other side products are mainly of BZ.

observation of other unknown side products percentages (Tables 4, 5, and 6, entry 7), along with an increase of conversion and a decrease of the control selectivity. Furthermore, after 6 h at the same temperature (70 °C), the chemoslectivity was reduced continuously to be 87%, 82%, and 85% of BA with CrLA1, CrLA2, and CrLA3, respectively, as recorded in Tables 4, 5, and 6, entry 8.

We can deduce here that the catalytic oxidation of benzyl alcohol by an aqueous H_2O_2 is catalyzed by CrLA1, CrLA2 or CrLA3 influenced by temperature.

Nevertheless, at 80 °C, both the selectivity and the conversion percentages were highly observable, enhanced, and progressed up to 93%, 85%, and 74% of BA with optimized chemoselectivity (100%) (i.e., no presence of BZ or other
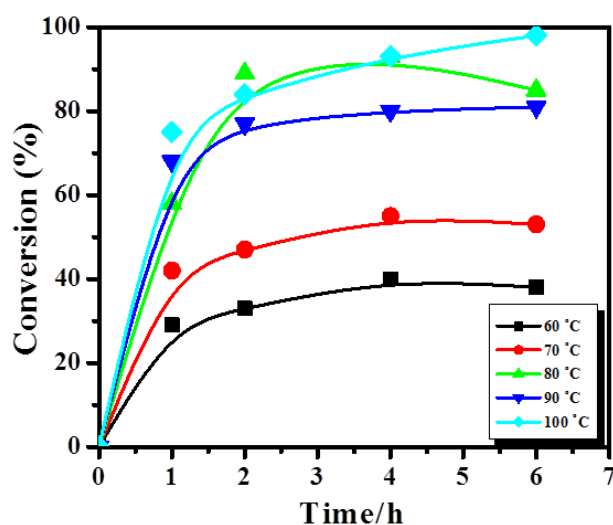
Figure 2: Effect of temperature and time on benzyl alcohol oxidation by H_2O_2 and catalyzed by CrLA1.

Figure 3: Effect of temperature and time on benzyl alcohol oxidation by H_2O_2 and catalyzed by CrLA2.

unknown side products for CrLA1, CrLA2 or CrLA3, resp., as shown in Tables 4, 5, and 6, entry 8). GC results supported the observation of residual amount of A with CrLA1, CrLA2, and CrLA3 (7%, 15%, and 36%, resp., as shown in Tables 4, 5, and 6, entry 11). Hence, the optimization for the catalytic potential of CrLA1, CrLA2 or CrLA3 as a homogeneous catalyst for the oxidation of A to BA by an aqueous H_2O_2 is at 80 °C after 4 h with excellent conversion (93%, 85%, and 74%, for CrLA1, CrLA2, and CrLA3, resp.) and excellent chemoselectivity for all catalyst Cr(III)-complexes (100%) (Tables 4, 5, and 6, entry 11).

Unfortunately, after further time (6 h) at the same temperature, the chemoselectivity to BA was reduced and the conversion was improved awarding mixture of BA and BZ, with no deduction of other unknown side products (Tables 4, 5, and 6 of CrLA1, CrLA2, and CrLA3, resp., entry 12). After 6 h, the percentage of BA was highly reduced to be 75%, 69%, and 60% with improvement of BZ percentage to be 21%, 21%, and 9% (Tables 4, 5, and 6, entry 12) within CrLA1, CrLA2, and CrLA3, respectively.

Particularly, at 90 °C after 1 h (Tables 4, 5, and 6, entries from 13 and 16), the catalytic potential of CrLA1, CrLA2 or CrLA3 was excellent with low chemoselectivity to BA. The conversion was poor to award to 45%, 41%, and 37%, respectively. With further time (i.e., after 2 h, 4 h or 6 h) the control chemoselectivity reduced remarkably and the conversion increased as recorded from TON and TOF values in Tables 4, 5, and 6, entries 14, 15, and 16, respectively. This could be explained by the further oxidation of the desired product, BA, to BZ and other unknown and unwelcomed side products.

The same behavior was also observed at 100 °C for all catalyst complexes: CrLA1, CrLA2, and CrLA3. Low
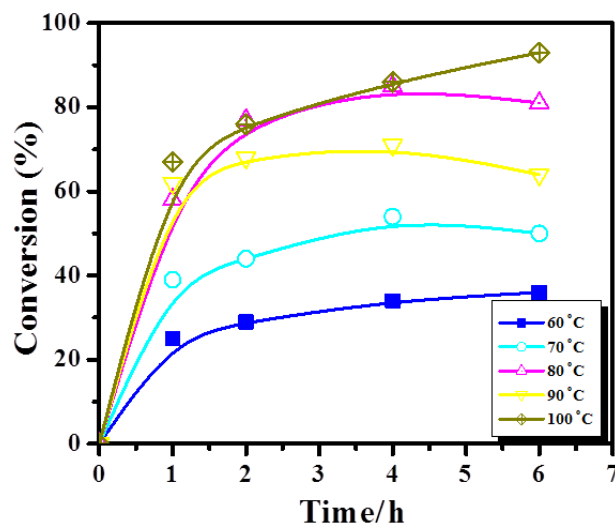
chemoselectivity and high uncontrol conversion are the results of the catalytic oxidation of R at 100 °C (Tables 4, 5, and 6, entries from 17 to 20). After 1 h, the yield of BA was good with presence of little amounts of BZ, unknown side products, and residual of the 13 reactants: 32%, 29%, and 26% of BA, 33%, 31%, and 28% of BZ, 10%, 7%, and 5% of other unknown side products, 25%, 33%, 41% of residual for CrLA1, CrLA2, and CrLA3, respectively (Tables 4, 5, and 6, entry 17). But by time, the amounts of the target product, BA, was decreased and, oppositely, the amount of BZ and the other unknown side products was increased as shown in Tables 4, 5, and 6 (entry 20) to reach at 6 h 15%, 13%, and 10% of BA, 60%, 57%, and 53% of BZ and 25%, 23%, and 19% of the other unknown side products for CrLA1, CrLA2, and CrLA3, respectively.

Figures 2, 3, and 4 show the conversion percentage of the benzyl alcohol oxidation by an aqueous H_2O_2 catalyzed by CrLA1, CrLA2 or CrLA3 at various temperatures and various times (Tables 4, 5, and 6 for CrLA1, CrLA2, and CrLA3, resp.). From Figures 2, 3, and 4, the highest uncontrolled conversion was at 100 °C affording 98%, 93%, and 82% of the reactant (R) oxidation using CrLA1, CrLA2, and CrLA3, respectively (Tables 4, 5, and 6, entry 20), with very low amount of the chemoselective product. On the other hand, at 80 °C, the oxidation process presents that the highest percentage of the chemoselectivity and the lowest of side products and reactant is awarded after 4 h (Tables 4, 5, and 6, entry 11) using CrLA1, CrLA2, and CrLA3; see TON and TOF values in Tables 4, 5, and 6. In particular, it could be concluded that the optimized oxidation process of benzyl alcohol to the target product BA by an aqueous H_2O_2 catalyzed by CrLA1, CrLA2 or CrLA3 is at 80 °C. Conclusively, all the above catalyst complexes have excellent
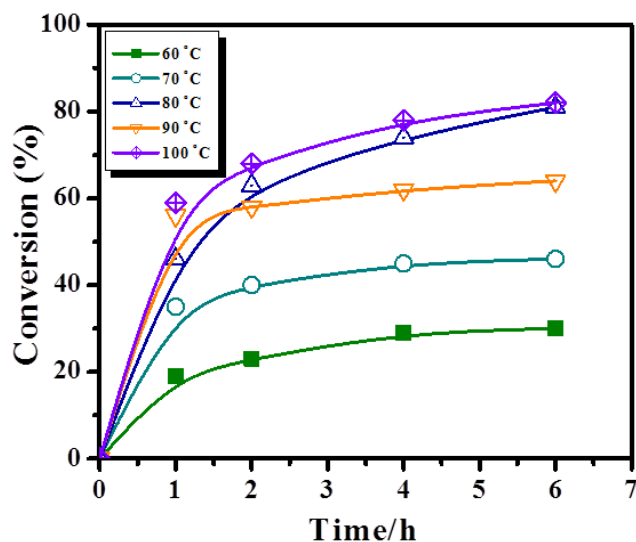
Figure 4: Effect of temperature and time on benzyl alcohol oxidation by H_2O_2 and catalyzed by CrLA3.

catalytic activity for oxidation of benzyl alcohol under the optimized catalytic conditions to benzaldehyde.

3.2.2. Effect of catalyst type and their backbone

The solubility of the catalyst complex plays an essential role in the catalytic activity in a homogeneous system, as observed elsewhere [26, 31, 32]. Hence, the attached backbone coordinated ligand, polarity, and solubility of the current Cr(III)-catalysts may play a remarkable role for their catalytic potentials for the benzyl alcohol oxidation by H_2O_2 solution based on structure-activity relationship [33].

From the tentative Cr(III)-complex chemical structures (cf. Scheme 1 and [23]), the main difference in the chemical structure between CrLA1 and CrLA2 is the aromatic derivatives (i.e., *o*-ethoxy phenyl and naphthyl derivatives, resp.). It is already well known that naphthyl group is more organic in nature than the *o*-ethoxy phenyl group. Hence, CrLA1 has more nature than CrLA2 because of the naphthyl group and so it is more soluble in the oxidation process in acetonitrile as the organic solvent (acetonitrile). This suggestion increases the possibility that the oxidation reaction of benzyl alcohol catalyzed by CrLA1 is more homogeneous compared to that reaction catalyzed by CrLA2 [34]. This probability could be acceptable due to the solubility of CrLA1 and CrLA2 in acetonitrile. Moreover, the position of nitrate ion as a coordinated ligand in CrLA1 and as a counter ion in CrLA2, could allow the behavior of CrLA2 as a complex cation (Scheme 1) and reduces, particularly, its solubility in the organic solvent. So, the oxidation process could be more heterogeneous in nature in that solvent. This observation supports also the little higher catalytic activity of CrLA1 compared to CrLA2 in the oxidation process. The

high observable difference between CrLA1 and CrLA2 in solubility and also in the catalytic potentials could be tough in the yield percentages of the chemoselective product for the oxidation of R to BA (93% and 85% of BA catalyzed by CrLA1 and CrLA2, resp.).

Generally, CrLA1 and CrLA2 are more reactive catalysts than CrLA3. To explain this behavior, the type of the coordinated ligands to the central metal ion, Cr(III) ion, may be the main reason. In CrLA3, the ligand behaves as a tetradentate chelate, while, in CrLA1 and CrLA2, the ligands are tridentate. Cr(III) ion forms octahedral geometric structures in CrLA1, CrLA2, and CrLA3 with coordination number 6; as shown in the tentative chemical structure of the studied complexes (Scheme 1). CrLA3 is more close and the ligand surrounds and capsulates Cr(III) ion to isolate it and afford more stable and less soluble complex (CrLA3) in polar organic solvents; whereas CrLA1 and CrLA2 are less stable than CrLA3 and more soluble in polar organic solvents (e.g., in methanol, acetone, and acetonitrile). Those reasons may be the main factors influencing the catalytic reactivity of the Cr(III)-imine complexes on the oxidation of benzyl alcohol to BA by an aqueous H_2O_2. Additionally, the presence of a labile coordinated solvent molecule in the catalyst complex (water as an open coordination site), as reported in many previous works [26, 32], is playing an obvious role in the enhancement of the catalytic reactivity of the Cr-catalysts. This will be discussed in the mechanistic pathways. The presence of a labile coordinated water molecule in CrLA1, CrLA2 or CrLA3 may improve their catalytic activity (Scheme 2), but the steric demand of the coordinated imine ligands, as tridentate in CrLA1 and CrLA2 and as tetradentate in CrLA3, may play a major role in measuring the catalytic potentials of the studied Cr(III)-catalysts. The backbone ligand as more bulky with more steric demand influence in CrLA3 has less catalytic activity compared to CrLA1 and CrLA2 with the less bulkiness and steric demand. The main explanation is that studying of the mechanistic steps revealed that CrLA3, being more bulky and having more steric demand, reduced the availability of the substrate (R) or the oxidant (H_2O_2) to approach to the central metal ion, Cr(III) ion, in order to coordinate, forming a less stable active intermediate (see the reaction mechanism) [26]. On the other hand, CrLA1 and CrLA2 that are less bulky and have less steric demand are highly reactive towards oxidation of benzyl alcohol by an aqueous H_2O_2 for approaching and coordinating of the substrate (R) or oxidant with Cr(III) to proceed the oxidation process.

3.2.3. Effect of solvents

Many transition metal complexes are considered as high effective catalysts for such redox processes. The strong impact of the nature of the involved organic or inorganic
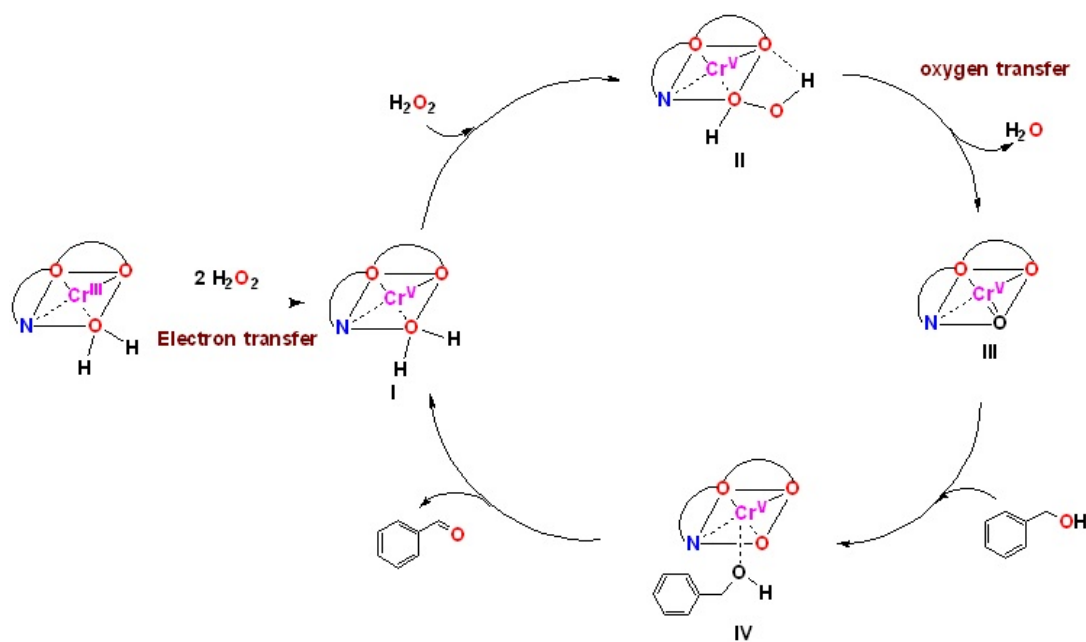
Scheme 2: Proposed mechanistic pathway for the oxidation of benzyl alcohol by an aqueous H_2O_2 solution catalyzed by Cr(III)-imine complexes.

solvent could be observed in such benzyl alcohol oxidation processes recently [35, 36, 37]. The influence of various solvents with different organic nature (i.e., acetone, dichloromethane, chloroform, and DMF (N,N′-dimethyl formamide)) on the oxidation of benzyl alcohol by H_2O_2 catalyzed by Cr(III)-imine complexes was investigated and summarized in Table 7.

Under the optimized reaction conditions of the highest active Cr(III)-catalyst complexes (CrLA1, CrLA2 or CrLA3), the effect of acetone, dichloromethane or chloroform was subjected and investigated. The results in Table 7 illustrate the percentages of the conversion control and chemoselectivity of R to BA. Particularly, the trend of the observed solvent effect was ordered as follows: acetonitrile > acetone > dichloromethane > chloroform > DMF for all Cr(III)-complex catalysts. In acetone, the control conversion percentages were good after acetonitrile (67%, 57%, and 51% of BA with CrLA1, CrLA2, and CrLA3, resp.) with unremarkable percentages of BZ. The oxidation in dichloromethane afforded moderate amount of the target product of BA using all Cr(III)-catalyst complexes with observable resulted amounts of other unknown side products (31%, 39%, and 31% using CrLA1, CrLA2, and CrLA3, resp.; cf. Table 7). In chloroform, the catalytic reactivity of all catalyst complexes was low with high uncontrolled conversion and with low chemoselectivity to BA. Particularly, the percentage of BA in chloroform is 25%, 24%, and 15%, using CrLA1, CrLA2, and CrLA3, respectively. Considerably, in DMF, there was on observation by GC for BA or BZ production in the

oxidation process, the only products detected are unknown side products with very high percentages (cf. Table 7).

It is rationalized that the chemoselectivity of the catalytic oxidation of benzyl alcohol in those solvents is very poor with excellent uncontrolled conversion and unselectivity, compared to that in acetonitrile.

The polarity of the various solvents in the catalytic oxidation of alcohols may play an effective role for the chemoselectivity and conversion [26, 32]. In the highest polar solvent, acetone, the reactivity of all Cr(III) catalyst complexes CrLA1, CrLA2, and CrLA3, which afforded 67%, 57%, and 51% of BA, respectively, is overall good with detection of BZ and unknown side products. The catalytic potential of Cr(III) complexes is lower in acetone than in acetonitrile. Also, the conversion percentages of the oxidation process with all Cr(III) catalysts are the same percentages in acetonitrile, but the chemoselectivity in acetonitrile is higher than that in acetone (cf. Table 7). This may be attributed to the high solubility and polarity of CrLA1, CrLA2, and CrLA3, which progressed their catalytic potential but reduced their control and chemoselectivity. The effects of solubility and polarity of the Cr(III) catalysts could be realized in the less polar solvents, dichloromethane. The catalytic potential was very low with conversion in dichloromethane (53%, 40%, and 36% of BA) and chloroform (25%, 24%, and 15% of BA) with CrLA1, CrLA2, and CrLA3, respectively; see Table 7. The low solubility of the current catalysts may be the reason for their low reactivity in the less polar solvents (i.e., in chloroform and dichloromethane). Finally, in the high

Table 8: Effect of catalyst amount on the catalytic activity of benzyl alcohol oxidation using Cr(III) complexes at optimum conditions.

Catalyst	Catalyst (mmol)	Yield (%)[a]				Conversion (%)	Selectivity (%)
		BA[b]	BZ[c]	Side product	R		
CrLA1	0.02	93	—	—	7	93	100
	0.05	65	32	—	3	97	67
	0.10	45	35	20	—	100	45
CrLA2	0.02	85	—	—	—	85	100
	0.05	51	37	—	12	88	67
	0.10	41	33	19	7	93	47
CrLA3	0.02	75	—	—	25	75	100
	0.05	48	21	2	21	79	61
	0.10	37	28	20	15	85	44

[a]The oxidation of benzyl alcohol (BZ) (1.0 mmol) catalyzed by Cr(III) complexes with aqueous H_2O_2 (3.00 mL) in 10 mL solvent for 4 h at 80 °C.
[b]The yield based on GC results, selectivity percentage of the target oxide product BA.
[c]The other side products are mainly of BZ.

coordinated solvent, DMF, the studied complex catalysts are inactive in the chemoselectivity for the oxidation of R to BA; as reported previously [26].

It is assumed that in aprotic solvents (e.g., acetonitrile) the catalytic potential of CrLA1, CrLA2, and CrLA3 is highly chemoselective compared to the other solvents (Tables 4, 5, and 6). It is also rationalized that the most effective solvent for the alcohol oxidation processes is acetonitrile; as reported elsewhere [11].

3.2.4. Effect of catalyst amount

The effect of the catalyst was discovered by injection of different molar ratios of the catalysts (CrLA1, CrLA2, and CrLA3) in the benzyl alcohol in the oxidation process (0.02 mmol, 0.05 mmol or 0.10 mmol) using H_2O_2 in acetonitrile at 80 °C for 4 h (the optimized reaction conditions). In other words, the effect of the amounts of the catalysts is related to the amount of the substrate (benzyl alcohol) on the oxidation processes with 0.02 : 1, 0.05 : 1 and 0.10 : 1 (catalyst: benzyl alcohol). The results are reported in Table 8. The catalytic potentials of CrLA1, CrLA2, and CrLA3 at a catalytic amount of 0.02 mmol have been studied and reported in Tables 4, 5, and 6. The increase of the catalyst molar ratio to 0.05 mmol and 0.10 mmol caused improvement in the rate of benzyl alcohol oxidation with higher conversion compared to the catalytic amount 0.02 mmol of the Cr(III)-imine complexes. Unfortunately, the chemoselectivity was reduced by increasing the amount of the catalyst Cr(III)-imine complexes to be 67%, 57.9%, and 61% of benzaldhyde with CrLA1, CrLA2, and CrLA3, respectively (at 0.05 mmol).

When the catalytic amount of the catalyst increased to the double amount (0.10 mmol) of the catalyst complexes, their catalytic activity was more reduced to the chemoselective target product, as 45%, 44%, and 43.5% using CrLA1, CrLA2, and CrLA3, respectively (Table 8).

Although the increase of the catalyst complexes of the Cr(III) unit amounts (from 0.02 mmol to 0.05 mmol and 0.10 mmol) enhanced the reaction rate and the catalysts reactivity, it did not incubate the control chemo- and stereoselectivity of conversion. It increased the further benzyl alcohol oxidation to other unknown side products (Table 8).

3.2.5. Proposed catalytic mechanism

It was observed that the presence of a labile coordinated solvent ligand in the complexes of Cr^{III} (Scheme 2) may generate Cr^V (structure I) intermediate within electron transfer process due to the interaction of the oxidant with the catalyst complex as previously observed [26, 38, 39, 40, 41, 42]. Particularly, the detection of Cr(V) intermediate species in the reaction media (structure II) has taken place by monitoring the repeated electronic spectral scans of complex in the oxidation process (Figure 5). The intensity of the characteristic maximum absorption bands are little shifted during the reaction. That little shift in the intensity of the characteristic absorption bands depends upon the addition of the oxidant to the catalyst complex in the reaction media. That little shift is probably due to the formation of active species in the oxidation reaction by the replacement of the coordinated labile solvent molecule (water molecule in structure I) with the oxidant molecule (i.e., H_2O_2 (structure II)) in order to form an oxide intermediate (structure II) within coordination of the oxidant to the central metal ion [43, 44]. Several studies have been reported that the oxo-chromium(V) complexes are probably the intermediates in the oxidation processes of various organic compounds catalyzed by Cr^{III} complexes [38, 39, 40, 41, 42]. Hence, the Cr^V=O active species are formed through the oxygen transfer mechanism from the coordinated oxidant molecule to give the active intermediate (structure III) with extraction of a water molecule [14]. The change in the color of the reaction in the beginning of the catalytic
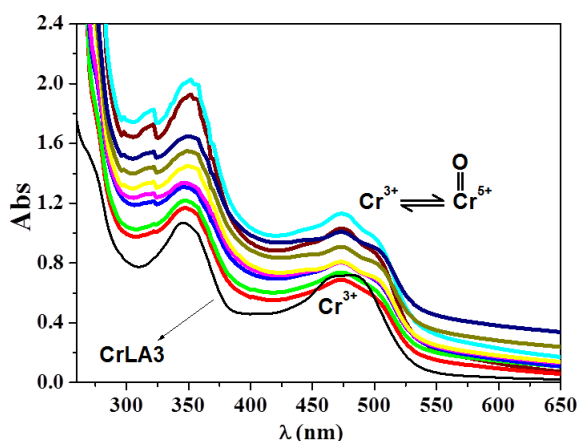
Figure 5: Repeated electronic spectral scan changes of CrLA3 catalyst with benzyl alcohol in the presence of an aqueous H_2O_2 in acetonitrile at 80 °C.

oxidation process initial solution from light green to brown highly supports the suggestion for the oxygen transfer from the oxidant (H_2O_2) to the central metal ion (Cr^V) to form oxo-chromium(V) species (structure III in the mechanistic proposal). When an aqueous H_2O_2 was added to the solution, the color slowly changed to brown. The observed change may be due to the generation of $Cr^V=O$ species. This behavior expresses the interaction of peroxido group of the coordinated oxidant with Cr^V center ion and the presence of strong charge transfer transition in the new product (structure III). The active oxo-chromium(V) intermediate could oxidize the substrate (benzyl alcohol) through the coordination of benzyl alcohol to the active oxo-chromium(V) intermediate (structure IV) to regenerate the oxidized catalyst complex intermediate (structure I) and award the chemoselective product (i.e., benzaldehyde). Generally, the summarized mechanism of the catalytic processes for Cr^{3+}-species is not enough clear [26]. However, on the basis of the color changes through the catalytic system of the reaction mixture and depending on the reported mechanisms for such reactions [38, 39, 40, 41, 42, 45, 46], it could be predicted here that the key step is the oxo-chromium(V) species formation in the catalytic process through the oxidation reaction of alcohols, as shown in Scheme 2, and as reported elsewhere [45, 46].

4. Conclusion

Imines are widely employed as versatile ligands for the preparation of highly stable chelates with Cr(III) ion. The preparation and characterization of mononuclear Cr(III) imine chelates is described here and previously mentioned. Due to the tri- and tetradentate chelating features of H_2LA1, H_2LA2, and H_2LA3, they coordinated to Cr(III) ion with the formation of octahedral geometry. The catalytic sufficiency of these complexes was estimated in the oxidation of

benzyl alcohol using an environmentally friendly oxidant, H_2O_2. They were used as homogeneous catalysts with green oxidant, H_2O_2, for the benzyl alcohol oxidation. CrLA1 shows an excellent catalytic activity compared to those of CrLA2 and CrLA3. The influence of alternative applicable parameters in the catalytic processes, including the molar ratio of catalyst to substrate, the temperature, and the solvent, has been examined to optimize the catalytic conditions. The optimal catalytic enhancement of Cr-imine catalysts was detected in acetonitrile at 80 °C. From the different molar ratios of the homogeneous catalyst to substrate, we concluded that enhancing the catalyst molar ratio from 0.02 mmol to 1.00 mmol causes improvement in their catalytic potential conversionally with inhibition of their selectively. The influence of some organic solvents with different polarity could be observed by the trend as acetonitrile > acetone > dichloromethane > chloroform > DMF. The mole polar solvent with high dielectric constant improves the catalytic processes within electron and oxygen transfer mechanism.

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