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Physicochemical studies on the desulfurization process of organosulfur compounds occur in crude oil by metallo-complexation method

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Abstract

All over the world researchers in accelerating to development the new and modern methods of desulfurization process to overcome the presence of residual sulfur compounds in the crude oil, which has harmful effects and undesirable. Out of these important research aims to use various copper(II) salts as catalysts to break the bond between the carbon and sulfur in thiourea compound as one of the initial organic compounds containing the sulfur element, which is present in many of the organic compounds present in crude oil. In literature survey at room temperature the chemical reactions between thiourea and different copper(II) salts give copper(II) complex with octahedral geometry and molecular formula as $[Cu(NH_2CSNH_2)_6]X_2$ where $X = CI^{-}$, Br^{-} , CH_3COO^{-} , NO_3^{-} , SO_4^{--} . The novelty of our study is precipitated yellow sulfur element and black copper(II) sulfide at elevated temperature ~90 °C through the molar ratio 1:6 (Cu⁺⁺: thiourea) in aqueous media. The infrared spectra of the resulted precipitated product clearly indicate the absence of bands due to thiourea. The scanning electron microscopy (SEM) and X-ray energy dispersive spectrometer (EDX) are scanned to check the morphological surfaces and the basic elements constituting the reaction products. A chemical mechanisms discussing the formation of sulfur and copper(II) sulfide are suggested.

Keywords: Desulfurization; infrared spectra; copper(II) ions; thiourea; SEM; EDX.

1-Introduction

The variuos transition/non-transition metal complexes of thiourea as rich donating chelation exhibit an interesting efficiency for biological activity including anticancer [1], antimicrobial [1-3], antibacterial [4], antifungal [5], antimalarial [6] and anti-tuberculosis [7]. Many scientific researchers were studied the coordination chemistry of benzoyl-substituted thioureas and related ligands toward metals where the ligand usually coordinated via sulfur and oxygen atoms, giving a six membered ring moiety [3-5]. These chelations able to coordinated to as neutral ligands or as anionic ligands with arrange metal centers [8-10]. The cobalt(II) complexes of thiourea derivatives form tetrahedral geometry with general formula CoL_2X_2 (where X= nitrate or acetate; L= thiourea derivatives) [11].

The desulfurization processes have been developed in order to removal of the inorganic sulfur from coal before combustion [12], but on the other hand, these methods have not been successful to removing organic sulfur such as thiophenols, and thiophenes [13-15] which predicted formed from organic sulfur component of coal. Commonly, there are no official methods and no basic documents in the chemistry of organic sulfur compounds depending on chemical reagents and conditions helpful in the oxy-desulfurization processes (oxidation of sulfur) [12-16]. However, the first oxidizing process for the organic sulfur compounds was accomplished by enhanced chemical reactivity of functionalities of electrophilic reagents (e.g., sulfoxides, sulfones, and sulfonic and sulfinic acids) in the presence of molten alkali (KOH or NaOH) [17]. Desulfurization processes of different organic sulfur moieties (e.g., benzothiophenes derivatives) were one of the most interesting topics in petroleum and chemical industries because of their application in the reduction of environmental pollution by desulfurization of coal fuels [18-22]. It is worth mentioning that the desulfurization of benzothiophenes derivatives converted to biphenyl have been discussed, but these reactions taken times [23, 24], high temperatures [25–27], and low yields [28]. The desulfurization processes of both dibenzothiophene sulfoxide and dibenzothiophene sulfone [29-33] using oxidizers agents [27] have been discussed. Morales, et. al., [34] were described new desulfurization methodology for the dibenzothiophenes derivatives (dibenzothiophene sulfoxide and dibenzothiophene sulfone) using lithium and sodium mixture to produced a high yield of biphenyl as shown in formula 1.



Formula 1: Desulfurization of dibenzothiophene, dibenzothiophene sulfoxide and dibenzothiophene sulfone organosulfur compounds using sodium-lithium mixture.

The hydrodesulfurization treatment process was discussed as a one of techniques helpful in the removal of organic sulfur existed in the petroleum fuels to reach the good quality of sulfur levels. The chemical mechanism of this method depend on the conversion of organosulfur compounds to hydrogen sulfide in the presence of some transition metal ions as a powerful catalyses which produced metal sulfides and liberated of hydrogen gas [35]. The cleavage of the bond between C–S atoms is an important aim to scientists working in the field of petroleum industrial, for example the hydrodesulfurization process of thiophene and its derivatives was a target to removal of sulfur impurities in petroleum ore [36-38] to achievement the satisfied environmental levels. Some articles [39-41] were focused on the using of transition metal complexes as probe catalyses in the carbon-sulfur bond. The rhodium dimmer, binuclear iridium, palladium and nickel(II) organmetallic complexes [42-44] have been successful in C–S cleavage process for dibenzothiophene and related compounds see formula 2.



Formula 2: The C–S cleavage process for dibenzothiophene using rhodium hydride dimmer complex

This research paper aimed to use thiourea as a model for organosulfur compounds which containing sulfur element that is non-desirable exhibited in petroleum fuels and trying to removal of sulfur by cleavage of C–S bond using copper(II) salts as an interesting catalysts.

2- Experimental

2-1-Synthesis

Reagent and chemicals are in high grade and used without purifications. In a six 250 mL volumetric flask thiourea (4.62 g, 60 mmol) was dissolved in deionized water (100 mL). To these was added 10 mmol of dissolved/suspended of CuCl₂, CuSO₄, Cu(CH₃COO)₂, Cu(NO₃)₂, CuBr₂ or CuCO₃ in 10 mL deionized water. The mixtures were heated at reflux for 15 h. The yellow and/or black precipitations of sulfur or copper sulfide compounds were filtered and washed several times with hot water then dried at 70 °C in an oven for 3 h till constant weight. The yields were in ratio 60-67 %.

2-2- Instruments

The elemental analyses of carbon, hydrogen, nitrogen and sulphur contents were performed using a Perkin Elmer CHN 2400 (USA). The content of copper metal was determined using iodometric titrations [45]. The infrared spectra with KBr discs were recorded on a Bruker FT-IR Spectrophotometer (4000–400 cm⁻¹). Scanning electron microscopy (SEM) images were taken in Quanta FEG 250 equipment and Energy Dispersive X-ray Detection (EDX) was taken in Joel JSM-6390 equipment, with an accelerating voltage of 20 KV.

3- Results and discussion

At room temperature, there are number of thiourea-metal complexes have been investigated [46] and it was found that the first class of metals studied (Pt, Pd, Zn, and Ni) form M-S bonds, since the C-N bond stretching frequency increases and the C-S bond stretching frequency decreases upon coordination without an appreciable change of the v(NH) stretching frequency. Using the same criterion, thiourea complexes of Fe(II), Mn(II), Co(II), Cu(I), Hg(II), Cd(II), and Pb(II) were also shown to be S-bonded [47, 48]. The only metal that is reported to be N-bonded in its complexes with thiourea is titanium (IV) [49]. The octahedral copper(II) thiourea complex [Cu(TU)₆]²⁺, (TU= thiourea; formula 3) has been prepared and investigated [47, 48].



Formula 3: The octahedral copper(II) thiourea complex $[Cu(TU)_6]^{2+}$ at room temperature

The chemical reactions in aqueous solutions between thiourea and $(CuCl_2, CuSO_4, Cu(CH_3COO)_2, Cu(NO_3)_2, CuBr_2 \text{ or } CuCO_3)$ salts with 1: 6 (copper(II) salt: thiourea) molar ratio at ca. ~90 °C formed a yellow and black solid precipitations for the (CuCl_2, CuSO_4, Cu(CH_3COO)_2, or Cu(NO_3)_2) and (CuBr_2 or CuCO_3) salts reacted with thiourea, respectively. The infrared spectral bands of the solid precipitated materials are represented in Fig. 1A-G. These IR bands have not been recorded any bands assigned to coordinated thiourea, also, there are no absorption bands in the infrared spectra of copper(II) thiourea systems at elevated temperature. This strongly confirms that the reactions were completely finished and the reaction products are yellow sulfur and black copper(II) sulfide. This paper shows a significant point for the pathways to get the copper(II) sulfide salt and sulfur element in a pure grade and simple procedures. It is difficult to generalize the result, which was obtained on all transition metal salts,

but we can say that the metals and their different ions have an important role in the control outputs of chemical reactions. This fact has been confirmed in this paper where we found that the chloride, nitrate, acetate, and sulfate ions, all gave pure yellow sulfur while bromide and carbonate ions gave copper(II) sulfide black. Generally, we can review the role of the copper metal ions as a catalyst to break the bond between the carbon and sulfur atoms in a thiourea compound briefly illustrated by the following reaction mechanisms;

1- Reaction mechanism to form copper(II) sulfide

i-
$$6(NH_2)_2CS + 12H_2O \xrightarrow{90 \ ^{O}C} 6(NH_4)_2S + 6CO_2$$

ii- $6(NH_4)_2S + 6CuX_2 \xrightarrow{90 \ ^{O}C} 12NH_4X + 6CuS (ppt)$
(Where: X= Br or CO₃)

2- Reaction mechanism to form sulfur
i-
$$6(NH_2)_2CS+12H_2O+ nH_2O \xrightarrow{90 \ ^{O}C} 6(NH_4)_2S + 6CO_2 + nH_2O$$

ii- $6(NH_4)_2S+6CuX_2 + nH_2O \xrightarrow{90 \ ^{O}C} 12NH_4X+6CuS + nH_2O$
iii- $12NH_4X+6CuS + nH_2O \xrightarrow{90 \ ^{O}C} 2[Cu(NH_3)_6].2X_2 + 6H_2S + 4[Cu(H_2O)_6].4X_2 + nH_2O$
iv- $2[Cu(NH_3)_6].2X_2 + 6H_2S + 4[Cu(H_2O)_6].4X_2 \xrightarrow{90 \ ^{O}C} 2[Cu(NH_3)_6].2X_2 + 6H_2 + S (ppt) + 4[Cu(H_2O)_6].4X_2$
(Where: $X_2 = Cl_2$, SO₄, (CH₃COO)₂ or (NO₃)₂)

Subsequently, in the reaction mechanism to form copper(II) sulfide and pure sulfur element, thiourea was hydrolyzed by water molecules to form ammonium sulfide and carbon dioxide, which further reacted with copper(II) ions to form copper sulfide compound and ammonium salts. Furthermore, the third and fourth steps in case of reaction mechanism to form sulfur element, the formation of two soluble copper(II) complexes as $[Cu(NH_3)_6].2X_2$ and $[Cu(H_2O)_6].4X_2$ play an essential role for the hydrodesulfurization treatment to liberate hydrogen gases and remain sulfur residue. The X-ray powder diffraction patterns of the titled compound resulted from the chemical reactions between copper(II) bromide or carbonate with thiourea at

~90 °C in aqueous media with 1:6 molar ratio (Cu⁺⁺: thiourea) was indexed with the copper(II) sulfide structure (JCPDS: 24-0060). The SEM image of CuS and S element are shown in Fig. 2 and shows copper sulfide particles in the range of 1 μ m in diameter.

EDX spectra in Fig. 3 confirmed the presence of copper and sulfur in the samples formed from the reaction of $CuCO_3$ and $CuBr_2$, while EDX recorded only sulfur element in case of the reaction between $CuCl_2$, $CuSO_4$, $Cu(CH_3COO)_2$ or $Cu(NO_3)_2$ and thiourea.

4- Conclusions

This article was introduced simple, effective and cheap method for the desulfurization of thiourea compound. This study is a paved road for a lot of studies that can be used with sulfur compounds to break the bond between the carbon and sulfur and get rid of the harmful effects caused by environmental pollution with sulfur.

SCR



Fig. 1: Infrared spectra of A: thiourea, and B: CuBr₂, C: CuCO₃, D: CuCl₂, E: Cu(NO₃)₂, F: Cu(CH₃COO)₂ and G: CuSO₄ thiourea reaction products at 90 $^{\circ}$ C.

.0













Fig. 2: SEM images of A: CuBr₂, B: CuCO₃, C: CuCl₂, D: Cu(NO₃)₂, E: Cu(CH₃COO)₂ and F: CuSO₄ thiourea reaction products at 90 $^{\circ}$ C.











Fig. 3: EDX spectra of A: CuBr₂, B: CuCO₃, C: CuCl₂, D: Cu(NO₃)₂, E: Cu(CH₃COO)₂ and F: CuSO₄ thiourea reaction products at 90 $^{\circ}$ C.

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Highlights

- Copper(II) salts used as catalysts
- Desulfurization of thiourea compound in aqueous media using simple, effective and cheap method.
- This experimental method study the break bond between the carbon and sulfur.
- A chemical mechanisms discussing the formation of sulfur and copper(II) sulfide.

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