Aqueous Phase Reduction of Cr (VI) by Sodium Sulphide: A Kinetic, Thermodynamic and Stoichiometric Approach

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Abstract: The ability of Na$_2$S. 9H$_2$O to reduce Cr(VI) in aqueous phase was determined spectrophotometrically at different temperatures of (298 – 323 K) to study the effect of temperature on reduction while, the effect of pH was studied at pH 3, 5, 7, 9 and 12. The effect of concentration was also considered by varying the concentrations of the reductant (i.e. 1.67x10$^{-2}$, 2.5x10$^{-2}$, 3.33x10$^{-2}$, 4.17x10$^{-2}$ and 5x10$^{-2}$ mM) over a pH of 5 and 9 at 298 K and 5 minutes with concentration of Cr(VI) set at 1.9X10$^{-4}$ mM. The temperature effect showed that the reaction rate increased slightly with increase in temperature. The kinetic results showed that the reaction was Pseudo first – order with respect to Cr(VI) with the rate equation of $\frac{2d[Cr(IV)]}{dt} = k [Cr(VI)]$. The activation entropy obtained from plots of ln(k$_{obs}$/T) vs. 1/T was -197.53 J.K$^{-1}$mol$^{-1}$ agreeing with an associative mechanism of reaction. The activation enthalpy varied from (-7.5x10$^{-6}$ - 3.3x10$^{-6}$) kJmol$^{-1}$ and in most cases it was negative showing that the reaction was rather exothermic. The activation energies obtained were 58.87, 60.84; 62.82, 63.80 and 65.78 kJmol$^{-1}$ for the respective Kelvin temperatures of 298, 308, 318,323 and 333. This increase in activation energy with increasing temperature implied that bond breakage and product formation was more favourable at lower temperature. The stoichiometry therefore suggested that the Cr(VI) : Na$_2$S. 9H$_2$O molar ratio was 1: 0.75 Cr(VI), this value was found to be in agreement with the theoretically obtained result. The findings from the research show that Na$_2$S. 9H$_2$O could be used for the reductive detoxification of Cr(VI) in polluted areas.

Keywords: Aqueous phase Reduction, Cr(VI), Na$_2$S.9H$_2$O

1. Introduction

The utilization of different mineral resources obtained from the earth’s crust has no doubt lead to technological and economic advancements. These exploitations have in turn created serious environmental discomfort some of which are life threatening and others lethal. So many metals have been extracted from their ores and explored for one application or the other and one of such metals is chromium.

Chromium (Cr) is the only elemental solid which shows antiferromagnetic ordering at or below room temperature [1]. It also has high corrosion resistance and hardness. Many of its compounds are intensely coloured. Because of its unique characters and for these unique attributes, Cr is widely used in electroplating, tanning, pigments, dyes, industrial water cooling, metal finishing, magnetic tapes, paper pulp producing, photographic film, automotive parts, chemical manufacturing, wood protection, ore and petroleum refining, metallurgical and refractory producing, and other industrial activities [2], [3]. Due to these industries and other anthropogenic activities (e.g. disposal of products or chemicals containing Cr, or burning of fossil fuels), huge amounts of Cr compounds have been discharged into the environment, including air, soil, and water [4], [5].

In nature, Cr exists in numerous oxidation states between -2 to +6, but only Cr(III) and Cr(VI) are stable. It is interesting to note that these two forms of Cr exhibit very different toxicities and mobilities. Cr(VI) usually occurs as highly soluble and toxic chromate anions (HCrO$_4^-$ or CrO$_4^{2-}$) and is a suspected carcinogen and mutagen. In our previous article [6], it was stated that Cr(VI) exposure in humans can induce allergies, irritations, eczema, ulceration, nasal and skin irritations, perforation of eardrum, respiratory track disorders and lung carcinoma. Moreover, Cr(VI) evidences the capability to accumulate in the placenta, damaging fetal development. Cr(VI) pollution in the environment alters the structure of soil microbial communities, reducing microbial growth and related enzymatic activities, with a consequent persistence of organic matter in soils and accumulation of Cr(VI) hence the need for reduction of Cr(VI) by suitable and environmentally benign reducers.

Cr(III) on the other hand is an essential element in mammalian metabolism. In addition to insulin, it is used to reduce blood glucose levels and control certain cases of diabetes. It is also responsible for reducing blood cholesterol levels by diminishing the concentration of low density lipoproteins “LDLs” in the blood [7], [8]. Various chemicals have been used as model reductants for Cr(VI) detoxification in contaminated sites as elucidated elsewhere [9] - [12].

2. Materials and Methods

2.1 Preparation of Solutions

All solutions were prepared using distilled water. All glass wares and plastics were washed with distilled water, rinsed with (1:1) HNO$_3$ and finally with distilled water. Cr(VI) stock solution was prepared from commercially obtained K$_2$Cr$_2$O$_7$ (BDH) by dissolving 2.828g of the salt in 1 L of distilled water. A 2 mg L$^{-1}$ Cr(VI) solution was prepared measuring exactly 2 mL of the stock solution in 1 L of distilled water. Na$_2$S. 9H$_2$O stock solution was prepared by
dissolving 1.0 g of the salt in a litre of distilled water. Interferences were avoided by adding diphenyl carbazide to Cr(VI) before adjusting the pH of the solution.

2.2 Experimental Procedure

Cr(VI) reduction by Na₂S, 9H₂O was conducted in accordance with the method described elsewhere [5], [13], [14] with slight modifications. A 10 mL portion of 3.85x10⁻² mM Cr(VI) was measured into a 250 mL beaker and a 20 mL aliquot of 8.3X10⁻² mM Na₂S, 9H₂O was added and the mixture shaken thoroughly. The pH of the solution was adjusted using 1.0 M H₂SO₄ in the acidic region and 1.0 M NaOH in the alkaline region before they were made to come in contact. The UV/Visible spectrophotometer (Milton Roy USA Spectronic 20D) was set at 349 nm and the absorbance of Cr(VI) was read at that wavelength where the absorbance of Na₂S, 9H₂O was found to be weak. The set up was done in triplicate at temperatures of 298, 308, 318, 323 and 333 K. In order to study the effect of rate on Cr(VI) reduction, separate set ups of the above mixture were made and each monitored for different time intervals of 0, 1, 2, 3, 4 and 5 minutes to minimize interference due to withdrawal of samples. The reaction was done for the initial pH values of 3, 5, 7, 9 and 12.

The stoichiometric study was conducted using five concentrations of the reductants: 1.62x10⁻², 2.5x10⁻², 3.33x10⁻², 4.17x10⁻² and 5x10⁻² mM to assess the concentration – dependence of the reaction. The reaction was at 298 K and a moderately acidic pH of 5 and an alkaline pH of 9. The initial concentration of Cr(VI) was set at 1.92x10⁻³ mM and the reaction time was 5 minutes. Equal volumes of 10 mL each of the reductant and Cr(VI) was used for the mixture.

3. Results

3.1 Kinetic Study

Figures 1 – 5 presents the results obtained from the plots of ln[Cr(VI)] vs time for the reduction of Cr(VI) by Na₂S, 9H₂O at various temperature and pH. Generally speaking, the reaction followed a pseudo – first order kinetic pattern with dependence on the concentration of Cr(VI) in solution. After monitoring the reactions at physiological temperature (298 K), the reactions were further considered at higher initial temperatures of 308, 318, 323 and 333 K. The reactions were observed to be faster as the temperature of the reaction was increased most of the reaction were completed at a temperature of about 308 K and at a time of 180 seconds. The observed rate constants (kobs) were obtained from these plots and it was observed that, the rate of reduction was basically increasing with decrease in pH. The rate of reduction was also slightly affected by increase in temperature with most reaction reaching completion at 180 seconds when the initial temperature was increased to 308 K. The rate in acidic and neutral solutions was faster than in basic solution. This observation agreed with that of Bill et al., [15] where an in situ kinetic reduction of Cr(VI) by ferrous iron in solid phase was studied. The findings of the present study are also to be consistent with those of Wittbrodt and Palmer, [16] and Elovitz and Fish, [17]. When the pH was kept at 3, the kobs was found to be 0.98, 1.02, 1.05, 1.07 and 1.1 s⁻¹ for 298, 308, 318, 323 and 333 K respectively. But when the pH was adjusted to 5, the kobs became 0.78, 0.82, 0.85, 0.86 and 0.89 s⁻¹ for the respective Kelvin temperatures. The trend did not change when the pH was modified to 7 as the kobs further decreased to 1.02 x 10⁻², 1.06 x 10⁻², 1.09 x 10⁻², 1.11 x 10⁻² and 1.14 x 10⁻² s⁻¹ for 298, 308, 318, 323 and 333 K respectively. At pH 9 and 12, a similar trend of 7.89 x 10⁻³, 8.15 x 10⁻³, 8.41 x 10⁻³, 8.55 x 10⁻³, 8.81 x 10⁻³ and 1.10 x 10⁻², 1.20 x 10⁻², 1.00x10⁻², 1.70 x 10⁻², 1.80 x 10⁻³ s⁻¹ respectively was obtained for 298, 308, 318, 323 and 333 K respectively. The reason for this trend is ascribable to the fact the dominant Cr(VI) species are HCrO₄⁻ at pH 1-6 and CrO₇²⁻ at pH > 6. Cr(VI) also forms other species, such as HCr₂O₇²⁻ and Cr₂O₇²⁻. However, their formation requires Cr(VI) concentrations > 10⁻² mol·dm⁻³. The increase in reaction rate with decreasing pH can therefore probably be attributed to HCrO₄⁻ which is reduced more easily than CrO₇²⁻ [18].

The Cr(III) oxidation state is the most stable as seen in the Frost diagram in Figure 7. Energy would be required to convert it to lower or higher states. The negative standard redox potential (E₀) of the Cr(III)/Cr(II) metal ion couple signifies that Cr(II) is readily oxidized to Cr(III), and Cr(II) species are stable only in the absence of any oxidant [23]. The reduction potential of Cr(II) is -0.90V and that of Cr(III) is -0.74 V [24].

3.2 Thermodynamic study

In order to study the thermodynamic activation parameters, the kobs obtained from the plot of ln[Cr(VI)] vs time was divided by temperature and fit into the following Eyring’s equation;

\[
\ln \left( \frac{kh}{kBT} \right) = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{2}
\]

Where:
\( \Delta H \) = the activation enthalpy (J mol⁻¹)
\( \Delta S \) = the activation entropy (J K⁻¹mol⁻¹)
\( R \) = the gas constant (8.314 J K⁻¹mol⁻¹)
\( T \) = the absolute temperature (Kelvin)
\( k \) = the rate constant (s⁻¹)
\( h \) = the Planck constant (6.63 x 10⁻³⁴ Js)
\( k_{B} \) = the Boltzmann constant (1.38 x 10⁻²³ J K⁻¹)

The Eyring’s equation was used to make a plot of

\[
\ln \left( \frac{k_{obs}}{T} \right) vs \frac{1}{T}
\]

as seen in Figure 8 and the activated entropy (\( \Delta S^0 \)) was obtained at the intercept of the plot while the activated enthalpy (\( \Delta H^0 \)) was obtained from the slope. The
results obtained from the plots revealed that the activated entropy was a large negative value of \(-197.5321 \text{ J K}^{-1}\) and the activated entropy had a value of \(-1.66 \times 10^{-6} \text{ J mol}^{-1}\) for all temperatures. The implication of the large negative value of the \(\Delta S^*\) is that the reaction followed an associative mechanistic pathway \([5]\), \([6]\), \([13]\).

Figure 1: A plot of \(\ln [\text{Cr(VI)}]\) against time (seconds) at pH 3

Figure 2: A plot of \(\ln [\text{Cr(VI)}]\) vs time (seconds) at pH 5

Figure 3: A plot of \(\ln [\text{Cr(VI)}]\) against time (seconds) at pH 7

Figure 4: A plot of \(\ln [\text{Cr(VI)}]\) vs time (seconds) at pH 9

Figure 5: A plot of \(\ln [\text{Cr(VI)}]\) vs time (seconds) at pH 12

Figure 6: Cr standard redox potential in both acid and basic solutions (Source: \([13]\))
Figure 7: The Frost diagram for chromium species in Acidic solution (Source: [20])

Figure 8: A plot of $\ln(K_{ob}/T)$ vs $1/T$

The activation energy was calculated from the relationship

$$E_a = \frac{T\Delta S}{(3)}$$

$$E_a (kJ/mol)$$ is an operationally defined quantity expressing the dependence of rate constant on temperature according to equation 4

$$E_a = RT\left(\frac{ln k}{T}\right)$$

$$k = Aexp\frac{-Ea}{RT}$$ (5)

The Ea were 58.8664, 60.8399, 63.8029, and 65.7782 kJmol⁻¹ for 298, 308, 318, and 323 K respectively. When these values were compared with the results obtained elsewhere [13], it was observed that the Ea of organic reductants were higher compared to the one obtained when using Na₂S.9H₂O as a model reductant implying that the reaction was more favourable when using an inorganic reductant than the organic counterpart.

Table 1: Activation Data for Cr(VI) Reduction by Organic Compounds at 298 K

<table>
<thead>
<tr>
<th>Reductant</th>
<th>$\Delta S$ (kJ/mol)</th>
<th>$\Delta H$ (J/K/mol)</th>
<th>$E_a$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin C</td>
<td>62.5</td>
<td>71.0</td>
<td>63.5</td>
</tr>
<tr>
<td>Ethanol</td>
<td>84.8</td>
<td>120.2</td>
<td>85.3</td>
</tr>
<tr>
<td>Isopropyl alcohol</td>
<td>85.3</td>
<td>107.7</td>
<td>85.3</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>80.5</td>
<td>180.8</td>
<td>80.7</td>
</tr>
<tr>
<td>Triphenylcarbinol</td>
<td>80.7</td>
<td>105.0</td>
<td>80.7</td>
</tr>
<tr>
<td>Benzydrol</td>
<td>76.9</td>
<td>153.2</td>
<td>76.9</td>
</tr>
</tbody>
</table>

Source: [13]

3.3 Stoichiometric Study

It has been established that the reduction of Cr(VI) generates Cr(III) compounds [19] – [22]. Theoretical reactions between Cr(VI) and Na₂S.9H₂O result in the following stoichiometric equation [5]:

$$4CrO_4^{2-} + 32H^+ + 3S_2^2- \rightarrow 8Cr^{3+} + 3SO_4^{2-} + 16H_2O$$ (6)

When the reaction is conducted in an alkaline medium, the equation generated becomes as shown in equation (7):

$$3S_2^{2-} + 4CrO_4^{2-} + 16H_2O \rightarrow 3SO_4^{2-} + 8Cr^{3+} + 32OH^-$$ (7)

Reactions 6 and 7 show that the theoretical quantitative relationship between Cr(VI) and Na₂S.9H₂O does not change irrespective of the pH. When the reaction was assessed in an experimental condition, a similar trend was obtained as the amount of Cr(VI) consumed at pH 5 decreased in the same pattern as it was when the pH was changed to 9.

Table 2 below reveals the amount of Cr(VI) (mM) consumed when the concentration of Na₂S.9H₂O was varied at pH 5 and 9.

<table>
<thead>
<tr>
<th>S/No.</th>
<th>$[Na_2S_{9}H_2O]$ (mM)</th>
<th>$^{3}Cr(VI)$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.6x10⁻²</td>
<td>1.25x10⁻²</td>
</tr>
<tr>
<td>2</td>
<td>2.50x10⁻²</td>
<td>1.85x10⁻²</td>
</tr>
<tr>
<td>3</td>
<td>3.33x10⁻²</td>
<td>2.45x10⁻²</td>
</tr>
<tr>
<td>4</td>
<td>4.17x10⁻²</td>
<td>3.13x10⁻²</td>
</tr>
<tr>
<td>5</td>
<td>5x10⁻²</td>
<td>3.75x10⁻²</td>
</tr>
</tbody>
</table>

Table 2: Showing the variation of Cr(VI) as the concentration of Na₂S.9H₂O was varied at pH of 5 and 9

At first glance, it can be seen that the concentration of Cr(VI) consumed increased steadily as the concentration of Na₂S.9H₂O was increased, while that of the residual Cr(VI) decreased steadily with increase in the concentration of Na₂S.9H₂O. For example, when the concentration of Na₂S.9H₂O was kept at 1.67x10⁻² mM in both pH regimes, the amount of Cr(VI) consumed was 1.25x10⁻² mM and the residual Cr(VI) was 1.82x10⁻² mM, this gives a Cr(VI): Na₂S.9H₂O molar ratio of 1:0.75 which agreed with the value obtained in theory as seen in equations 6 and 7. When the concentration of Na₂S.9H₂O was varied to 2.50x10⁻² mM, the amount of Cr(VI) consumed also increased to 1.85x10⁻² mM and the molar ratio of 1:0.75 was still maintained. The increase in the amount of Cr(VI) consumed at both pH regimes when the amount of Na₂S.9H₂O was increased agreed with the law of definite proportion. The ratio did not change when the amount of Na₂S.9H₂O was increased to 3.33x10⁻² mM as the amount of Cr(VI) consumed increased to 2.45x10⁻² mM giving a similar stoichiometric ratio. When the molar concentration of
Na$_2$S.9H$_2$O was increased to $4.17 \times 10^{-2}$ and $5 \times 10^{-2}$ mM, the concentration of Cr(VI) consumed increased in the same sequence to $3.13 \times 10^{-2}$ and $3.75 \times 10^{-2}$ mM. The fact that the stoichiometric amount of Cr(VI) reduced when the concentration of Na$_2$S.9H$_2$O was varied in both acidic and alkaline media showed clearly that the stoichiometry of Cr(VI) reduction does not depend on pH.

4. Conclusion

This present research has demonstrated that Na$_2$S.9H$_2$O reduced Cr(VI) in aqueous phase, the reduction rate decreased with increasing pH and the activation entropy (∆S) of the reduction was largely negative with a relatively small value of the activation enthalpy (AH). This gave rise to a Gibb’s energy of activation that has a smaller value when compared with the activation energy obtained from the reduction of Cr(VI) by some organic compounds under similar experimental conditions. These observations are rather advantageous because, whereas organic compounds reduce Cr(VI) higher energy of activation, Na$_2$S.9H$_2$O reduced Cr(VI) with a lower energy of activation meaning that Na$_2$S.9H$_2$O is a better reductant which can be used for cleanup and will complete the process in shorter time. The reduction process further showed that the stoichiometry does not depend on pH.

Future prospects of the research will be to engage in the mechanistic studies of the reduction process to ascertain the nature of the products formed through Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Isokinetic studies of the reduction processes are also recommended as well as exhaustive studies on the compensation effects of the isokinetic temperature.

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different organic reductants and different oxide surfaces. 

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