ANALYTICAL PROPERTIES OF 2-OXIMINODIMEDONE DITHIOSEMICARBAZONE

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Summary—The synthesis and analytical properties of 2-oximinodimedone dithiosemicarbazone are described.

Thiosemicarbazones have been widely used for spectrophotometric determination of inorganic ions and their analytical applications have been reviewed. Monothiosemicarbazones with an electron-donating group in the α position and α-dithiosemicarbazones have been studied the most. In recent years, some β-dithiosemicarbazones have been studied as analytical reagents. In this paper, the analytical properties of 2-oximinodimedone dithiosemicarbazone \([5,5\text{-dimethyl-1,2,3-cyclohexanetrione-2-oxime-1,3-dithiosemicarbazone (ODDT)}]\) are presented.

The synthesis of ODDT is based on that of 2-oximinodimedone by reaction of sodium nitrite with dimedone, and subsequent condensation with thiosemicarbazide.

EXPERIMENTAL

Synthesis of ODDT

Dimedone (2 g) was dissolved in a solution of 10 g of sodium hydroxide in 30 ml of water and 30 ml of ethanol; 0.986 g of sodium nitrite was then added, the solution was cooled in a freezing mixture, and stirred while 4 ml hydrochloric acid (1 + 1) were slowly added. To this solution were added 7.6 g of thiosemicarbazide dissolved in 100 ml of water and 200 ml of ethanol, followed by sodium acetate until the pH was 5. The solution was stored for 2 or 3 days in the refrigerator and the solvent was then removed at 30°C under reduced pressure. Yellow crystals separated and were washed with ethanol and water (m.p. 182-4°C; yield 70%).

The samples were prepared in 25-ml standard flasks with 50-200 l.g of the ion, 5 ml of 0.1 N solution of ODDT in dimethylformamide, 5 ml of buffer solution, and dilution to volume with distilled water. The spectrum in the region 350-700 nm was recorded, with a reagent blank as reference. The stochiometries of the reactions were investigated by Job’s method and the molar ratio method.

RESULTS AND DISCUSSION

Solubility

The solubility of ODDT in several solvents at room temperature was determined by Wittmerberger’s method. ODDT is very soluble in dimethylformamide (192 g/l.), ethanol (10.1 g/l.), ethyl acetate (13.0 g/l.), methyl isobutyl ketone (9.2 g/l.) and 3-methyl-1-butanol (9 g/l.) and sparingly soluble in water, chloroform, carbon tetrachloride and cyclohexane.

Stability

A dilute aqueous solution of ODDT (6 × 10⁻³ M) at pH > 2 is reasonably stable and a 3 × 10⁻³ M solution is stable for 2 days if made in dimethylformamide and for a week if made in ethanol or 3-methyl-1-butanol.

Spectral characteristics

The infrared spectrum was obtained (KBr discs) and the bands (cm⁻¹) were assigned to the stretching vibrations of \(-\text{NH}\) (3320), \(-\text{OH}\), \(-\text{C=N}\) (3140-3200) and \(-\text{C=S}\) (1100). The NMR spectrum was obtained in DMSO-d₆, with tetramethylsilane as internal reference. The peaks (δ, ppm) were assigned as follows: 1.05 (α-CH protons), 3.75 (α-CH₂ protons), 8.05-8.40 (α-NH, α-NH₂ protons) and 11.3 (α-NHOH protons).

The ultraviolet absorption spectra for the reagent in water, ethanol, 3-methyl-1-butanol, methyl isobutyl ketone, ethyl acetate and dimethylformamide media showed similar maxima between 310 and 330 nm. The ultraviolet absorption spectra at various pH values are shown in Fig. 1.

Ionization constants

The ionization constants were determined by the Stenström and Goldsmith method at 20°C and ionic strength 0.1. The average results obtained were: \(pK_1 = 7.5\) (oxime group) and \(pK_2 = pK_3 = 11.5\) (C=S group thione-thiol tautomerism). The \(pK\) values...
**SHORT COMMUNICATIONS**

**Table 1. Characteristics of ODDT compounds**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Medium</th>
<th>(i_{\text{max}}) nm</th>
<th>(a_e)</th>
<th>Stoichiometry (ODDT:ion)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>pH &lt; 2</td>
<td>380</td>
<td>8.6 \times 10^3</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>Ni(II)</td>
<td>pH 5.5-7.5</td>
<td>380</td>
<td>7.2 \times 10^3</td>
<td>2:1 Orange</td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>pH 0-2</td>
<td>380</td>
<td>1.0 \times 10^4</td>
<td>3:1 Orange</td>
<td></td>
</tr>
<tr>
<td>Fe(II)</td>
<td>HCl 0.6-5M</td>
<td>565</td>
<td>9.8 \times 10^3</td>
<td>3:1 Violet</td>
<td></td>
</tr>
<tr>
<td>Fe(III)</td>
<td>HCl 1-6M</td>
<td>565</td>
<td>9.8 \times 10^3</td>
<td>3.5:1* Violet</td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>pH 9</td>
<td>435</td>
<td>5.9 \times 10^4</td>
<td>Brown</td>
<td></td>
</tr>
<tr>
<td>V(V)</td>
<td>pH &lt; 2</td>
<td>390</td>
<td>4.4 \times 10^3</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>Pd(II)</td>
<td>pH &lt; 2</td>
<td>380</td>
<td>4.9 \times 10^3</td>
<td>Yellow</td>
<td></td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>HClO₄, 0.4-1M</td>
<td>490</td>
<td>5.6 \times 10^3</td>
<td>3:2 Orange</td>
<td></td>
</tr>
<tr>
<td>IO₄⁻</td>
<td>HClO₄, 1-2M</td>
<td>390</td>
<td>3.0 \times 10^4</td>
<td>3:1 Yellow</td>
<td></td>
</tr>
<tr>
<td>BrO₃⁻</td>
<td>HClO₃, 0.75-2M</td>
<td>390</td>
<td>3.1 \times 10^4</td>
<td>3:1 Yellow</td>
<td></td>
</tr>
</tbody>
</table>

*0.5 for reduction to Fe(II) which then forms the 3:1 complex.

![Fig. 1. Absorption spectra of 6.25 \times 10^{-3}M ODDT at different pH values.](image)

**Qualitative tests**

The reactions of ODDT with 54 inorganic ions were tested at different pH values. ODDT reacts with Fe(II and III) to give a violet colour, Co(II), Ni(II) and Cr(VI) to give an orange colour, Mn(II) brown, and V(V), Cu(II), BrO₃⁻ and IO₄⁻, yellow. The most important results are summarized in Table 1. These are chelating reactions, e.g., with Ni(II), Co(II) and Fe(II), and redox reactions, e.g., with Cr(VI), IO₄⁻ and BrO₃⁻, which involve a two-electron mechanism in accordance with the general redox behaviour of bisthiosemicarbazones. The stoichiometry of the Fe(II)-ODDT complex is 1:3 metal:ligand. If we start with Fe(III), this ion is reduced by the reagent, to give the same complex as Fe(II).

Various organic solvents were tested as extractants for the ODDT compounds. The results are summarized in Table 2.

![Table 2. Extraction of ODDT compounds](image)

The stability, solubility in various solvents, absence of absorption in the visible region, and the results compiled in Tables 1 and 2 provide a basis for judging the potential analytical utility of ODDT as a chromogenic reagent, especially for the spectrophotometric determination of Fe(II), Co(II), Cr(VI), IO₄⁻ and BrO₃⁻, which will be the subject of further work.

**REFERENCES**