refluxed for 1 h, following which the solvent was removed by vacuum leaving a clear oily residue. This was triturated with hot alcohol; the inorganic salts were filtered and the filtrate again concentrated to an oil which crystallized on standing. An 800 mg yield (34%) of the hydantoin melting at 165-168° was obtained.


N-Phenylcarbamyl-α-ethylserine
α-Ethylserine (1 g, 0.00752 mole) was dissolved in an equivalent of 10 ml aqueous sodium hydroxide (3 ml) and about 20 ml of water. To this was added a slight excess of phenyl isocyanate (1.07 g, 0.01 mole). The mixture was shaken vigorously for 1/2 h and then filtered. Acidification of the filtrate with concentrated hydrochloric acid precipitated a white solid which was filtered, washed with water, recrystallized from ethanol–water, and dried. A 1.3 g (69%) yield of pure material melting at 150-152° was obtained. The compound is acidic and requires 1 mole of sodium hydroxide for neutralization; neutralization equivalent, found 264 (calcd. 252).


β-Phenyl-5-ethyl-5-hydroxynorleucine
A solution of 350 mg of N-phenylcarbamyl-α-ethylserine in 20 ml of 6 N hydrochloric acid was refluxed 1 h, then concentrated in vacuo until a precipitate began to form. A small amount of water (10 ml) was added; the mixture was cooled and filtered, and the precipitate was dried. A 220 mg yield (68%) of a product melting at 155-156° was obtained. Cyclization had occurred because the product is now neutral.


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STUDIES OF SODIUM CUPRATE(III) STABILITY

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We have recently completed a study of the stability of sodium dioxcuprate(III) in various alkali bases at several different base strengths. In no case did we find that the salt was stable in solution and, in fact, the half-life of the CuO32- ion was estimated to be only 25 s. Thus, it appears that tervalent copper can be present in aqueous solution only in the presence of large stabilizing anions such as periodate or tellurate (1–3) or in the presence of large concentrations of hypobromite (4).

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EXPERIMENTAL

One of the methods reported by Scholder and Voelskow (4) for preparing NaCuO₂ was modified and used throughout this study. This procedure involves oxidation of copper(II) hydroxide with sodium hypobromite in strong base, the sodium cuprate(III) precipitating as a reddish-brown precipitate.

All reagents used were C.P grade. The sodium hypobromite and microcrystalline copper(II) hydroxide used were prepared according to the procedure of Scholder and Voelskow (4). The analytical procedure used was a modification of Park's (5) method for determining Cu(II) in the presence of As(III). An ice-cold mixture of 30 ml of 3.3 N NaOH and 15.00 ml of standard 0.2 N arsenic(III) solution was added to a sample of about 0.15 g solid sodium cuprate(III). The mixture, which contained a fine precipitate of copper(II) oxide was diluted with 90 ml of ice-cold water and acidified with 15 ml of cold 12 N sulfuric acid. Excess arsenic(III) was determined by titration with standard cerium(IV) solution using ferrous orthophenanthroline as the indicator and osmium tetroxide as catalyst (meq Cu(III) = meq As(III) - meq Ce(IV)). Three grams of potassium acid phthalate was added to the solution and the pH was adjusted to 3.5 with concentrated ammonium hydroxide (28% NH₃). Ten grams of potassium iodide, dissolved in a minimum quantity of water, was added and the solution was titrated with standard sodium thiosulfate to a light-orange end point. Starch solution was used as the indicator. The number of equivalents of sodium thiosulfate used equalled the number of moles of copper.

The decomposition of sodium cuprate(III) may be represented by the following equation:

\[ 4\text{NaCuO}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{NaOH} + 4\text{CuO} + \text{O}_2. \]

In this study, we followed the rate of decomposition of solid sodium cuprate(III) in the presence of base using a Warburg apparatus (6). A small sample of NaCuO₂ was placed in a glass vial which was inserted in a Warburg flask containing a known volume of base. After the flask had come to equilibrium in a constant temperature bath, the contents of the vial were mixed with the base and the mixture was shaken vigorously until an equilibrium pressure reading was obtained. Oxygen pressure readings were taken as a function of time during the decomposition. When decomposition was complete the solution of base and copper(II) was acidified and the amount of copper(II) was determined iodimetrically. Decomposition of sodium cuprate(III) in 1 N NaOH by this technique was used to check the analytical method given above.

RESULTS AND DISCUSSION

Products prepared by the above procedure contained 95 to 99% of the copper as copper(III). As a check on the accuracy of the arsenic(III) method of analysis, duplicate analyses of the same sample of sodium cuprate(III) gave a ratio of copper(III) to total copper of 0.796 and 0.800 by the gas volume method and 0.796 by the arsenic(III) method. As a check on possible air oxidation of the arsenic(III) solutions a series of blank runs were performed. Under the conditions of the analysis dissolved copper(II) is an excellent catalyst for the air oxidation of arsenic(III). However, solid copper(II) oxide and decomposed sodium cuprate(III) produced a maximum of 0.5 mole % oxidation in 1 h.

Scholder and Voelskow report that moist sodium cuprate(III) decomposes slowly. Analysis of a sample prepared by the method previously given showed 10% decomposition when stored for 8 days at room temperature. A portion of the same sample stored at 5 °C showed only 1% decomposition in the same period. In an effort to both dry and purify the sodium cuprate(III), samples were leached with various solvents. With freshly dried ethyl alcohol, dioxane, and acetone extensive decomposition occurred. Ethyl ether caused a slight decomposition (about 6%) but did not remove any moisture from the solid. Sodium cuprate(III) samples dried in a vacuum desiccator using either Mg(ClO₄)₂ or silica gel showed partial decomposition (20 to 35%). However, once dried the sodium cuprate(III) did not show further decomposition when stored in a desiccator over silica gel for 2 months at room temperature. These results are consistent both with the results of Scholder and Voelskow, who report a partial decomposition on drying the solid, and with those of Klemm and Wahl (7), who report that dry solid potassium dioxocuprate(III) is stable.

The results of the study of the decomposition of sodium cuprate(III) in the presence
of base are given in Table I. Inspection of Table I shows that sodium cuprate(III) decomposes more rapidly when in contact with KOH than NaOH and that the extent of decomposition increases as base strength decreases. Further, as may be expected, decomposition is more rapid at room temperature than at 0 °C.

**TABLE I**

Decomposition rate of sodium cuprate(III) in base*

<table>
<thead>
<tr>
<th>Base</th>
<th>0.0 °C decompositions</th>
<th>25.2 °C decompositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>meq Cu present</td>
<td>Time (min) for 50% decomposition</td>
</tr>
<tr>
<td>Satd. KOH</td>
<td>0.630</td>
<td>None in 40</td>
</tr>
<tr>
<td>10 M KOH</td>
<td>0.664</td>
<td>14</td>
</tr>
<tr>
<td>7.5 M KOH</td>
<td>0.619</td>
<td>7</td>
</tr>
<tr>
<td>0.5 M KOH</td>
<td>0.878</td>
<td>5</td>
</tr>
<tr>
<td>0.01 M KOH</td>
<td>0.633</td>
<td>4</td>
</tr>
<tr>
<td>Satd. NaOH</td>
<td>0.773</td>
<td>None in 150</td>
</tr>
<tr>
<td>10 M NaOH</td>
<td>0.585</td>
<td>None in 150</td>
</tr>
<tr>
<td>5 M NaOH</td>
<td>1.00</td>
<td>100</td>
</tr>
<tr>
<td>Satd. LiOH</td>
<td>0.633</td>
<td>40</td>
</tr>
</tbody>
</table>

*In all cases 20.0 ml base was used.

Except in the case of decompositions in lithium hydroxide, the rate of O₂ evolution appears reasonably linear. In 10 M and saturated NaOH however, we observed a 10 min period in which essentially no decomposition occurs followed by a constant rate of O₂ evolution to the equilibrium pressure reading. In saturated LiOH at 25.2 °C, the rate of O₂ evolution is equivalent to that observed in 5 M NaOH up to a point corresponding to about 45% of the equilibrium O₂ pressure reading. The O₂ evolution rate then becomes progressively smaller so that complete decomposition in saturated LiOH requires 60 min compared to 20 min in 5 M NaOH.

Qualitative observations of the precipitates indicated that the decomposition rate was primarily influenced by the rate of solution. This observation is confirmed by the fact that saturated potassium hydroxide at both 0 °C and 25 °C in which NaCuO₂ was dissolving and decomposing gave no indication of Cu(III) in solution when we titrated a rapidly filtered portion of the NaCuO₂–base mixture with a known amount of excess As(III) followed by standard Ce(IV). More than 0.02 meq of copper(III) in solution with a solid sample containing 0.60 meq of copper(III) would have been detected. These results show that the cuprate(III) ion is so unstable in basic solutions that it can not have a half-life of more than a fraction of a minute.

Lister's study (3) of the rate of oxygen evolution in a copper(III) hypochlorite solution at 20 °C can be used to give a lower limit to the half-life of a copper(III) solution assuming that 4 moles of copper(III) give 1 mole of oxygen and that no hypochlorite complexes are present. At 20 °C Lister finds a rate of oxygen evolution of 0.25 ml of oxygen per minute for 2.77 X 10⁻³ moles of copper. This represents a half-life of about 25 s. This result is approximately the upper limit given by our experiments and would fix the half-life of cuprate(III) ion at about 25 s. However, Lister's results can also be explained by assuming that only a small fraction of the copper is present as copper(III), and that the rest of the copper is present as a hypochlorite complex.

Scholder and Voelskow have shown that solutions of copper(III) are stable in the presence of both excess base and excess hypobromite. This indicates that the hypobromite is either stabilizing the cuprate(III) ion by forming a complex ion or the rate of oxidation of copper(II) by hypobromite is greater than the rate of copper(III) decomposition.
NOTES 1237


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A PROTON MAGNETIC RESONANCE STUDY OF SODIUM 3,5,5-TRIMETHYL HEXANOATE

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Continuing with an investigation of molecular motion of fatty acids and their salts, we have examined the broad line nuclear magnetic resonance (n.m.r.) spectra of the sodium salt of 3,5,5-trimethyl hexanoic acid. A commercial sample of the acid was distilled at 1 atm. Most of the acid distilled over between 226 and 228 °C and a portion of this central cut was taken for neutralization with an alcoholic solution of reagent grade sodium hydroxide. The solvent was partially evaporated and the precipitated soap was filtered and dried for some 24 h under vacuum. The precipitate was crushed to a powder, packed into pyrex sample tubes, and heated in the tubes for a further 24 h at 200° under vacuum before the tubes were sealed off.

Spectra were obtained on a Varian dual purpose spectrometer mainly at 60 Mc/s, although a few were run at 40 Mc. The depth of modulation varied from 0.14 gauss (G) to approximately 1 G, but most spectra were run at 0.14, 0.24, or 0.38 G modulation. Line shape and width were not observed to depend on the depth of modulation, and more specifically they were independent of modulation depth over the range 0.14 to 1 G at liquid nitrogen temperature and at 154 °K. This fact provides evidence that the narrowing of the absorption signal between 100 and 160 °K is not a spurious effect caused by the presence of an impurity whose absorption signal narrows at this temperature and obscures the still broad absorption of the main substance. Increasing the depth of modulation to 1 G from 0.14 G should produce at least some change in line shape at 154 °K if there is a broad as well as a narrow component of absorption actually present in the spectrum (1). The temperature of the sample was controlled by passing heated air or tank nitrogen cooled by passage through a cryostatic bath over the sample which was held in a dewar vessel within the n.m.r. probe. The temperature was measured by thermocouples placed in the airflow both upstream and downstream from the sample.

Typical spectra are presented in Fig. 1, and line width and second moment are shown as a function of temperature in Fig. 2. Three steps are distinguishable in the decrease of each of these parameters. The first and most obvious step begins immediately above liquid oxygen temperature and continues to about 160 °K. The second step is marked by a clear decrease in line width between 450 and 470 °K and a levelling off of the second moment at approximately 1.2 G² at 470 °K after a gradual decrease from some 4.5 G² at 350 °K. At temperatures above the third step, which occurs sharply at 538 °K, the line width is determined by depth of modulation and field homogeneity, and the second

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