A novel synthesis of tetramethylammonium trioxylfluorochromate(VI)

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Reaction between tetramethylammonium fluoride (CH₃)₄NF and CrO₃ in 1:1 molar ratio in the minimum amount of dry acetonitrile gives tetramethylammonium trioxylfluorochromate(VI), (CH₃)₄NCrO₃F in very high yields. The compound has been characterized by elemental analyses and IR spectral studies. The advantages of the new method are discussed.

In the course of our investigation on the fluoro compounds of transition metals and in continuation of our studies on the use of tetramethylammonium fluoride (CH₃)₄NF as a fluorinating agent and because the trioxylfluorochromates compounds with different counter ions are used as oxidants in organic chemistry, we were prompted to synthesize (CH₃)₄NCrO₃F with a new method. Trioxylfluorochromates(VI) have been known for many years and many methods have been used to synthesize them. But, trioxylfluorochromate(VI) with the counter ion tetramethylammonium has not been synthesized so far. We used a direct and novel method for this synthesis.

Reagent grade CrO₃ was used and anhydrous tetramethylammonium fluoride (CH₃)₄NF was prepared by the method reported by Christe in 1990. In a typical preparation, trioxochromium, CrO₃, was dissolved in a minimum amount of dry acetonitrile in a glove box under the argon atmosphere. To this dark solution stoichiometric amount of powdered tetramethylammonium fluoride was added with stirring, maintaining the ratio of (CH₃)₄NF : CrO₃ as 1:1. The reaction was very fast but for the sake of ensuring completion of reaction stirring was continued for 1 hour and the product was separated with the addition of dry benzene followed by filtration.

The tetramethylammonium trioxylfluorochromate(VI) obtained is highly pure, orange-yellow compound (Table 1); yield, 98%. The compound is not very stable in moist air and like other trioxylfluorochromates can be stored in sealed polythene bags.

The IR spectra of the newly synthesized (CH₃)₄NCrO₃F recorded on a Shimadzu instrument model 420 have been compared with the corresponding reported data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cr</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₄NCrO₃F</td>
<td>24.52</td>
<td>6.42</td>
<td>7.21</td>
<td>27.2</td>
<td>9.6</td>
</tr>
<tr>
<td>(24.87)</td>
<td>(6.22)</td>
<td>(7.25)</td>
<td>(26.94)</td>
<td>(9.84)</td>
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</tbody>
</table>

The method used for the synthesis does not involve direct use of HF or reaction of MHF₂ (M = NH₄, K, Rb or Cs) with CrO₃ and is based on the concept of strong action of tetramethylammonium fluoride (CH₃)₄NF and its power to fluorinate many compounds. In other words, the method is based on the concept of the reaction of the naked fluoride ion of tetramethylammonium fluoride that is produced by the dissociation of tetramethylammonium fluoride in acetonitrile.

The reaction can be written as:

\[ \text{CrO}_3 + (\text{CH}_3)_4\text{NF} \rightarrow (\text{CH}_3)_4\text{N}[\text{CrO}_3\text{F}] \]

The advantages of the new method are as follows: (i) there is no side product, (ii) the reaction is quite fast and (iii) the accompanied colour change can be used to ascertain the completion of the reaction.

Tetramethylammonium trioxylfluorochromate(VI) is soluble in acetonitrile, acetone, dimethyl sulphoxide (DMSO) and common organic solvents but it is easily hydrolyzed in water. This compound decomposes when it reacts with ammonia wherein Cr(VI) is reduced to Cr(III) and its color becomes yellow.

Table 1—Characterisation data of tetramethylammonium trioxylfluorochromate(VI)
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References