LETTERS TO THE EDITOR

DIELECTRIC CONSTANTS OF THE SYSTEM \( X \text{Sm}_3\text{NbO}_7 + (1 - X) \text{La}_2\text{NbO}_7 \)

The structural properties of the above system have been recently reported.\(^1\) The aim of the present note is to study the dielectric properties of the system \( X \text{Sm}_3\text{NbO}_7 + (1 - X) \text{La}_2\text{NbO}_7 \) \((0 \leq X \leq 1)\). The dielectric constant \((\varepsilon)\) and loss tangent \((\tan \delta)\) were measured on circular pellets of 12 mm diameter and about 1-2 mm thickness by the same methods as described earlier.\(^2\) The results are shown in Table I.

<table>
<thead>
<tr>
<th>(X)</th>
<th>Structure type</th>
<th>Dielectric constant ((\varepsilon))</th>
<th>(\tan \delta \times 10^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>W</td>
<td>800</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>W</td>
<td>660</td>
<td>1.6</td>
</tr>
<tr>
<td>30</td>
<td>W</td>
<td>565</td>
<td>1.2</td>
</tr>
<tr>
<td>40</td>
<td>W</td>
<td>495</td>
<td>1.8</td>
</tr>
<tr>
<td>50</td>
<td>W</td>
<td>400</td>
<td>2.0</td>
</tr>
<tr>
<td>60</td>
<td>W</td>
<td>300</td>
<td>2.3</td>
</tr>
<tr>
<td>80</td>
<td>P + W</td>
<td>220</td>
<td>5.0</td>
</tr>
<tr>
<td>100</td>
<td>P</td>
<td>240</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*\(W = \text{Orthorhombic \text{Website type}}\), \(P = \text{Cubic \text{defect \text{fluorite (Pyroclore) type}}}\). See reference (1),

It may be seen that the \(\varepsilon\) and \(\tan \delta\) values go on decreasing with increasing \(X\). This seems to be connected with the strain in the lattice which goes on increasing with \(X\) till the critical value of \(X \geq 80 \text{ mole\%}\) is reached. It is also observed that at this critical composition the \(\varepsilon\) and \(\tan \delta\) values show a minimum and a maximum respectively. Similar observations have been previously recorded.\(^3\) The minimum value of \(\varepsilon\) (220) corresponding to the appearance of a cubic pyrochlore phase is comparable to that reported for \(\text{Pb}_2\text{Nb}_2\text{O}_7\), also crystallising with the pyrochlore structure \((\varepsilon = 185)\).\(^4\) The reason why the \(\varepsilon\) values seem to be related to the strain may be sought in the change in the covalent character of the A site cation \((\text{La}^{3+} \text{and Sm}^{3+})\) in the 12-fold co-ordination, this character increasing\(^5\) as the ionic size decreases \((\text{La}^{3+} = 1.14 \text{ Å}, \text{Sm}^{3+} = 1.00 \text{ Å})\).\(^5\) This increase in the covalent character seems to be associated with a decrease in the effective polarizability of ions at the A site as \(\text{La}^{3+}\)

\((5 \, d^1 \, 6 \, s^2)\) is slowly replaced by \(\text{Sm}^{3+}\)

\((4 \, f^6 \, 5 \, d^0 \, 6 \, s^2)\) and thereby resulting in a decrease in \(\varepsilon\) with \(X\).

Dept. of Physical and V. S. CHINCHOLKAR.
Solid-State Chemistry,
Institute of Science,
Nagpur, April 6, 1971.

1. Thakre, O. B., Patil, P. V. and Chincholkar, V. S.,
2. Chincholkar, V. S., Menezes, C. A. and Biswas, A. B.,
5. Schneider, S. J., Roth, R. S. and Waring, J. L.,

OXYMERCURATION-DEMERCURATION OF ACETYLENES

The oxymercuration reaction combined with the reduction of the oxymercural intermediate by sodium borohydride provides a convenient method to achieve Markownikov's hydration of carbon-carbon double bonds without any observable rearrangement.\(^1\) It has been shown\(^3\) that the strain in the olefin plays an important role in the mode of addition, e.g., cis-cyclooctene undergoes normal \textit{trans}-addition while \textit{trans}-cyclooctene gives \textit{cis}-addition product. Recently, it has been shown that the addition is not controlled by steric factors in the case of bicyclic olefin like 7,7-dimethyl-norbornene and it gives exclusively \textit{exo}-alcohol. A study has now been made to extend this reaction to representative acetylenes like 1-octyne, 3-hexyne, cyclotridecyn, phenylacetylene and diphenylacetylene to find the effect of the substituent on the yield of the ketone formed.

The acetylenes, 1-octyne, 3-hexyne, cyclotridecyn, phenylacetylene and diphenylacetylene were synthesized by known procedure and characterised by comparison of vapour phase chromatographic retention times and IR spectra with authentic samples. The respective acetylene (30 mmole) was oxymercured with mercuric acetate (30 mmole) in tetrahydrofuran (30 ml)-water (30 ml) system. The yellow colour of the reaction mixture disappeared in 20 seconds and it was stirred for 10 min at room temperature to complete the reaction. The demercuration of the respective oxymercural
TABLE I

<table>
<thead>
<tr>
<th>Acetylenes</th>
<th>Ketones</th>
<th>Melting point and mixed m.p. of 2:4-dinitrophenyl hydrazone</th>
<th>Percentage yield of ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1-Octyne</td>
<td>2-Octanone</td>
<td>56-57(^\circ)</td>
<td>70-0</td>
</tr>
<tr>
<td>2. 3-Hexyne</td>
<td>3-Hexanone</td>
<td>127-129(^\circ)</td>
<td>83-3</td>
</tr>
<tr>
<td>3. Cyclotrideyne</td>
<td>Cyclotridecanne</td>
<td>114-115(^\circ)</td>
<td>78-0</td>
</tr>
<tr>
<td>4. Phenylacetylene</td>
<td>Acetophenone</td>
<td>235-236(^\circ)</td>
<td>55-1</td>
</tr>
<tr>
<td>5. Diphenylacetylene</td>
<td>No reaction</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

(without isolation) was done by adding 30 ml of 3 M sodium hydroxide followed by 30 ml of 0.5 M sodium borohydride in 3 M sodium hydroxide. The recovery of the reaction product was carried out according to Moon and Waxman. The reaction mixture was neutralised by cautious addition of 3 M hydrochloric acid (just neutral). The water-tetrahydrofuran mixture was decanted from mercury and thoroughly extracted with benzene. The benzene layer was washed with water, separated and dried (anhydrous magnesium sulphate). After removal of the solvent, the residue was distilled under reduced pressure to obtain the reaction product. The ketones were characterised by their physical properties, vapour phase chromatographic analysis, IR spectra and determination of mixed melting points of 2:4-dinitrophenylhydrazone derivatives. The results are shown in Table I.

The formation of the ketones from terminal and internal acetylenes can be visualised as follows:

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\begin{align*}
R-C\equiv C-R + Hg(OA)c_2 & \xrightarrow{THF-H_2O} [R-C\equiv C-R] + HgOA_c \xrightarrow{H_2O} [R-C\equiv C-R] + OH \xrightarrow{NaBH_4} [R-C\equiv C-R] \xrightarrow{O H} [R-C\equiv C-R] \xrightarrow{H} [R-C\equiv C-R] \\
\end{align*}
\]

All the alkyl-substituted acetylenes underwent 100% conversion while phenylacetylene underwent conversion only up to 55.1%. Diphenylacetylene did not undergo oxymercuration reaction under similar conditions. This difference in reactivity could be dictated solely by the electronic factor. The steric effect seems to be of secondary importance in these reactions. Our results clearly point out that the electron-withdrawing power of phenyl group makes the acetylenic bond less prone to electrophilic attack by the electrophile Hg\(^+\)OAC.

The oxymercuration of cyclotrideyne provides a convenient method of synthesising cyclotridecanone as the synthesis of cyclotrideyne can be achieved in two steps starting from readily available cyclododecene.

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2. —, and Hammar, J., ibid., 1967, 89, 1524.

SOME HYDRAZONES OF 5-BROMO- AND 5, 7-DIBROMO-COUMARALIC ACID HYDRAZIDES AS POSSIBLE ANTITUBERCULAR AGENTS

With a view to study antitubercular activity, hydrazones of 5-bromo-, and 5, 7-dibromo-coumaralic acid hydrazides have been prepared. These hydrazides were obtained by the action of hydrazine hydrate on 5-bromo, and 5, 7-dibromo-2-carbethoxy coumarones. All the ketonic compounds, selected in this work, have hydroxyl group in ortho position. This may make a significant contribution to the activity because of the possibility of a chelate ring formation by hydrogen-bonding between the hydroxyl group and the terminal nitrogen of the hydrazones.

Experimental Section

5-Bromo-2-carbethoxy coumarone

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