Spectroscopic Study of the Monotropic Forms of Monochloracetic Acid

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Monochloracetic acid (CClH₂-COOH) is a trimorphic substance. Only one of the three forms is stable, viz.: the α form; whereas the β and γ forms are metastable. The infrared spectrum of the forms α and β has been studied; that of the γ form has not been studied because of its extreme instability.

It has been seen that the spectrum of the α form is different from that of the β form. The fundamental frequencies of monochloracetic acid have been assigned, bearing in mind the assignments made by the present authors in another paper for di- and trichloracetic acids.

This assignment makes it possible to determine that the displacements which are observed when passing from form α to β chiefly affect the frequencies bound up with the carboxyl group and more especially those in the OH group. This has been confirmed by the preparation of the deuterated derivatives which likewise present themselves in α and β forms, the same relative differences in frequencies being observed.

It is inferred from this study that the two crystalline forms differ in the structure of the intermolecular types of bonds. All these things can produce marked differences in the molecular spectrum.

Although as far back as 1910 Nyswander¹ began studies with the infrared spectra of calcite and aragonite, there is still no extensive bibliography in existence on the changes in the infrared spectrum produced by changes in crystal type. Very few papers refer to organic substances, among them 17-ethinylstradiol,² phthalo cyanines,³ para red,⁴ and glutaric acid.⁵

The authors of the present paper have studied the spectra of chloracetic acids and, in the case of monochloracetic acid, they have ascertained that, according to the conditions in which the sample solidified, variations appeared in the infrared spectrum.

It is generally known that monochloracetic acid is a trimorphic substance of the group of so-called monotrops, i.e., those in which the transformation of one variety into another can only occur in one direction, there being no equilibrium between two forms at any temperature. With nuclear magnetic resonance technique, even in extreme dilute aqueous solution, it was impossible to interpret the results in terms of a simple equilibrium between the two forms.⁶ At all tempera-

⁵ B. Bak (private communication).

SPECTROSCOPIC STUDY OF MONOCHLORACETIC ACID

TABLE I.

<table>
<thead>
<tr>
<th>Frequencies</th>
<th>Class</th>
<th>Assignment</th>
<th>aCClH₂COOH</th>
<th>aCClH₂COOD</th>
<th>dCClH₂COOH</th>
<th>dCClH₂COOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>222</td>
<td>A&quot;</td>
<td>T</td>
<td>243 cm⁻¹</td>
<td>242</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>127</td>
<td>A'</td>
<td>δ (CCl)</td>
<td>410</td>
<td>414</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>115, 117</td>
<td>A'</td>
<td>r (COOH)</td>
<td>422</td>
<td>424</td>
<td>454</td>
<td>448</td>
</tr>
<tr>
<td>100</td>
<td>A'</td>
<td>r (CCl₂)</td>
<td>554</td>
<td>520</td>
<td>546</td>
<td>523</td>
</tr>
<tr>
<td>158</td>
<td>A'</td>
<td>O</td>
<td>570</td>
<td>(561)</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>144</td>
<td>A'</td>
<td>δ (CCl₂)</td>
<td>650</td>
<td>614</td>
<td>660</td>
<td>625</td>
</tr>
<tr>
<td>123</td>
<td>A'</td>
<td>r (CCl₂)</td>
<td>795</td>
<td>792</td>
<td>800</td>
<td>795</td>
</tr>
<tr>
<td>115</td>
<td>A'</td>
<td>δ (OH)</td>
<td>845</td>
<td>640</td>
<td>875</td>
<td>655</td>
</tr>
<tr>
<td>100</td>
<td>A'</td>
<td>δ (CH₂)</td>
<td>940</td>
<td>935</td>
<td>940</td>
<td>940</td>
</tr>
<tr>
<td>94</td>
<td>A'</td>
<td>r (CH₂)</td>
<td>1190</td>
<td>1181</td>
<td>1195</td>
<td>1181</td>
</tr>
<tr>
<td>86</td>
<td>A'</td>
<td>r (CH₂)</td>
<td>1220</td>
<td>1052</td>
<td>1233</td>
<td>1065</td>
</tr>
<tr>
<td>86</td>
<td>A'</td>
<td>δ (CH₃)</td>
<td>1302</td>
<td>1301</td>
<td>1315</td>
<td>1317</td>
</tr>
<tr>
<td>86</td>
<td>A'</td>
<td>δ (C=O)</td>
<td>1425</td>
<td>1378</td>
<td>1407</td>
<td>1380</td>
</tr>
<tr>
<td>86</td>
<td>A'</td>
<td>r (C=O)</td>
<td>1702</td>
<td>1722</td>
<td>1713</td>
<td>1722</td>
</tr>
</tbody>
</table>

slowly at room temperature with a complete absence of α germs, we get the form β. By cooling to -20° or leaving it for a few days, or, better still, by sowing a small crystal of the α variety, we get the form α. These two forms have been obtained as crystals with a suitable thickness for the study of their infrared spectrum. We have also studied the Raman spectrum of the melted acid.

The deuterated monochloracetic acid was prepared by hydrolysis of the corresponding anhydride with deuterium oxide. The crystalline α and β forms of the heavy acid was prepared similarly to the light forms.

EXPERIMENTAL RESULTS

Table I shows the fundamental frequencies of monochloracetic acid, both light and heavy, in each case, for the two forms α and β. This table only covers the frequencies below 1800 K. The lowest frequencies are taken from the Raman spectrum and since they have been obtained from the melted acid only they are assigned to the α form. The other frequencies have been obtained from the infrared spectrum of the forms α and β.

In the table we give the numbered frequencies, their classes, the assignments, the value for the light α form (αCClH₂COOH), that for the heavy α form (dCClH₂COOD), that for the light β form (βCClH₂COOH), and that for the heavy β form (dCClH₂COOD).

Among the fundamental frequencies are also found the ν₂ 2956 K, class A₁, and the ν₁ 3007 K, class A₁/2, corresponding to the stretching CH vibrations, which can be easily observed in the Raman spectrum and in the infrared one of the β form, since in the one corresponding to the (light) α form they are overlapped by the wide band of OH···H. This band, which can also be considered fundamental, only appears in the α forms, with the frequency ~3100 K for the light acid and ~2290 K for the deuterated acid. The difference of the spectra belonging to this area in the case of the forms α and β of the light acid can be seen in Fig. 1, where the corresponding submaxima are also present.

DISCUSSION

The assignment of the frequencies of the stable form of monochloracetic acid was made elsewhere. For this assignment we have taken into account those of di- and trichloracetic acids done in a previous paper. Figure 2 shows the correlation of the assignments which have been made for the three chloracetic acids.

For monochloracetic acid, as for the other two, we presume a symmetry C₈, admitting that the plane of symmetry contains the two carbons, the chlorine and all the carboxyl group. Only the two H atoms are out

![Fig. 1. Spectrum (νOH region) of the monochloracetic acid.](image)
of the plane. The 18 vibrations are active in the Raman and in the infrared, there being 12 of class $A'$ and 6 of class $A''$.

To classify the modes of vibration we have taken into account that in the molecule we can distinguish the vibrations of the carboxyl group, those of the halogenated group, and the external or chain ones. Each group actually contained six vibrations. Instead of 18 generated group, and the external or chain ones. Each vibration allows us to see the changes which occur on passing from form $\alpha$ to $\beta$ and when, in each of these forms, the hydrogen of the carboxyl group is replaced by the deuterium.

The difference is more marked in the band corresponding to the $\nu(\text{OH})$. This band of the dimer carboxylic acids has been repeatedly studied. Information on this question has been furnished by Bratoz et al.\textsuperscript{10} and Fuson and Josien.\textsuperscript{11} Independently of the theories advanced to explain this fact, there is the experimental result that in monomer carboxylic acids (dilute solutions or vapors) the OH vibration appears with a narrow band about 3500 K, but when there is an association, this band acquires a great breadth and shifts its maximum to 3000 K. It is also interesting to note that at the side of this broad band there appear a series of less intense bands, which some authors call submaxima.

All these phenomena are clearly apparent in the spectrum of the $\alpha$ form (Fig. 1), where a broad band is seen, followed by the corresponding submaxima. It should be pointed out that the two bands at 3035 K and 2956 K which are observed in lower concentrations correspond to the CH valence vibrations and have no bearing on the discussion of different crystal forms. In the spectrum of this region (Fig. 1) for the $\beta$ form the broad band has wholly disappeared, the two bands corresponding to the CH remaining, and the submaxima persist, although we observe that they have not exactly the same wave numbers.

It is quite clear that the passage from form $\alpha$ to $\beta$ produces the disappearance of the broad band and alters the frequency of the submaxima. This would seem to be connected with a variation in the form of the bond of the polymers which occur through the hydrogen bonds.

As is well known, the deuteration shifts this band to 2290 K, making it less broad but accompanied by submaxima. This is clearly apparent in the spectrum of the deuterated $\alpha$ form; but in the $\beta$ form this broad band also disappears, although its place is filled by some submaxima, which can also be seen in the $\alpha$ form.

Although the most obvious change in the spectrum appears in the vibration band of the OH group, as will be seen from Table I, there are also other changes which are observed from one crystalline form to the other. These, it will be observed, mainly affect the frequencies related to the carboxyl group. The lower frequencies have been observed only in the Raman spectrum of the melted acid, in which, we presume, the $\alpha$ form exists and, therefore, in the table we can give no values for the $\beta$ form. These lower frequencies have been assigned to the torsion and to the deformation of the C—Cl. Although we have no data on the $\beta$ form, the fact that there is no variation in deuteration shows that these frequencies bear no relation to the carboxyl group. On the other hand their low values are in line with the assignments.

There are two frequencies which are very interesting to study. The first one of them we have assigned to the

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two rockings of the $-\text{COOH}$ group, and the second, to the rocking of the $-\text{CCH}_2$. On studying the table it is seen that the first one is shifted on passing from form $\alpha$ to $\beta$, whereas in deuteration there is no shift. As regards the second, on the contrary, there is no great difference in the passage from from $\alpha$ to $\beta$, but there is a great difference in deuteration. These two assignments are the most doubtful ones.

The symmetric rocking of the $\text{CCIH}_2$ group only appears in Raman and there does not seem to be any shift in deuteration, as was to be expected.

The deformation of the Group $C\quad \text{O}$ has a small deformation of the $\alpha$ form to $\beta$ (10 K) and a greater deflection in deuteration, the difference remaining when passing from form $\alpha$ to deuterated $\beta$.

The frequency $\nu \text{Cl}_2$, as was to be expected, undergoes no change on passing from from $\alpha$ to $\beta$, nor in deuteration.

The out-of-plane OH deformation is shifted on passing from form $\alpha$ to $\beta$, and also in deuteration.

The frequency assigned to $C-\text{C}$ does not change either through the action of the crystalline form or through deuteration, as was to be expected.

The twisting of the $\text{CH}_2$ shows a slight difference in the forms $\alpha$ and $\beta$, but is not altered in deuteration. It is worth mentioning that the intensity of this band in the light and heavy $\alpha$ form is much below what it is in form $\beta$.

The frequency corresponding to the in-plane OH deformation differs by 15 K for the forms $\alpha$ and $\beta$, and undergoes a considerable shift in deuteration.

The frequency $\delta \text{CH}_2$ is not altered by deuteration, but it presents differences between the forms $\alpha$ and $\beta$, which is something more difficult to interpret.

The $\nu \text{C}-\text{O}$ frequency shows a shift both on passing from forms $\alpha$ to $\beta$, and on passing from the light to the heavy acid. This frequency, according to Hadzi and Sheppard,\textsuperscript{15} is closely bound up with that which appears about 1200 K, attributed to the $\delta \text{OH}$; it undergoes shift in deuteration. It is worthy of mention that the passage from form $\alpha$ to $\beta$ produces a shift in the contrary direction to those observed at other frequencies related to OH. Generally speaking, passage from form $\alpha$ to $\beta$ increases the frequency; but in this case there is a drop. In the light $\alpha$ acid, this occurs at 1425 K and in the $\beta$ it corresponds to 1407 K, which surprisingly does not occur in the case of the heavy acid forms.

Something similar occurs with the frequency corresponding to the $\nu \text{C}==\text{O}$ group, which remains the same, practically, in deuteration, whereas in the case of the light acid there are differences between form $\alpha$ and $\beta$.

This comparative study carried out between the frequencies of the $\alpha$ and $\beta$ forms of monochloracetic acid clearly proves that the difference between the spectra of these two forms is real. The difference appears clearly in the frequencies corresponding to the $-\text{COOH}$ group and more especially in those related to the OH group, which is corroborated by the study of the spectrum of the deuterated acid in the two forms.

There remain, however, a few points that are difficult to clarify. One is the assignment of the rocking frequencies of the two groups which form the acid, i.e., the $-\text{COOH}$ and $-\text{CCH}_2$, together with the shift, though small, of the $\delta \text{CH}_2$ and the $\nu \text{CH}_2$ bands in deuteration. The difficulties inherent in the $\nu \text{CO}$ band have already been dealt with by other authors.

The spectroscopic study of forms $\alpha$ and $\beta$ of monochloracetic acid has helped to explain their differences; and, at the same time, these differences have made it possible to improve the assignation of frequencies, with the added help of knowledge of the spectra of the other chloracetic acids and that of deuterated monochloracetic acid in its two crystalline forms.

Two polymorphic forms which show an equal infrared spectrum must have no intra or intermolecular differences; but when these differences appear in the spectrum they must be attributed to changes of this nature. Thus, the $\alpha$ and $\beta$ forms of monochloracetic acid must show differences in their molecular structures. Since the variations affect the frequencies related to the carboxyl group, it is in the latter that these differences must be sought, rather than in the position of the halogen in space, as other authors have thought.\textsuperscript{13}

It is logical to think that if the $\alpha$ form shows the broad band about 3000 K, characteristic of the hydrogen bonds usually belonging to the dimer structure,

\[
\begin{align*}
\text{O} & \cdots \text{H} \cdots \text{O} \\
\text{CCH}_2\text{C} & \\
\text{O} & \cdots \text{H} \cdots \text{O}
\end{align*}
\]

the latter must be the one corresponding to the $\alpha$ variety.

In the spectrum of the $\beta$ form the broad band is missing about 3000 K; but the submaxima remain and it is presumed they are related to the hydrogen bond. This leads us to suppose that in the $\beta$ form these does not exist the conventional dimer with double hydrogen bond. Since, as a general rule, the frequencies of the $\text{COOH}$ group have shifted at higher values, this would seem to show that they have greater freedom of movement, i.e., that the rigidness of the bond has disappeared, although the bond has not altogether disappeared, as is proved by the presence of submaxima, even though these are not in exactly the same position as in form $\alpha$.

It is not easy to assign a structure to this $\beta$ form. Tentatively we can suppose a breakup of the normal


bonds of the dimeric association giving a configuration of the type

\[
\text{O} \cdots \text{H} \cdots \text{O} \quad \text{CCl}_2 \text{-C}'' \quad \text{O-H} \cdots \text{O} \quad \text{C} \cdots \text{CCl}_2
\]

A similar structure has been reported by other authors for the dicarboxylic acids.

**ACKNOWLEDGMENT**

We thank Dr. F. Gomez Herrera from the Institute of Chemistry for his help in preparing the deuterated monochloracetic acid.

*Note added in proof.—This paper was presented on the Freiburg meeting of the European Molecular Spectroscopy Group in July, 1957. At this time we did not know the interesting paper of R. E. Kagarise [J. Phys. Chem. 61, 499 (1957)] that generally agrees with our results.*

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**Polarized Infrared Spectrum of Potassium Thiocyanate**

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The polarized infrared spectrum of crystalline potassium thiocyanate is reported in this paper. This additional information necessitates certain assignment changes in the observed vibrational frequencies from those previously reported. The vibrational spectrum now appears quite complete and in agreement with the crystal structure report of Klug.

**INTRODUCTION**

In a previous publication¹ the author presented an analysis of the vibrational spectrum and structure of crystalline KNCS. Though the combination and overtone bands yielded a rather complete analysis of the vibrational spectrum, there were certain unexplained anomalies in the intensities of some of the absorption bands. Since that time the author has obtained the polarized infrared spectrum of crystalline KNCS which necessitates certain assignment changes and removes the anomalies.

**EXPERIMENTAL**

Several attempts to grow crystals of suitable dimensions for polarized infrared studies were unsuccessful. A technique which was successful involved the following: a small amount of KNCS was heated above its melting point on a salt window (such as KBr), spread out in an even layer, and allowed to solidify slowly. In the majority of such attempts there occurred epitaxial growth of very small crystals. The spectrum of such samples showed a marked degree of polarization of the infrared absorption bands.

The spectra were observed on a Perkin-Elmer Model 112 spectrometer with LiF and CsBr prisms and on a Perkin-Elmer Model 21 spectrometer with rocksalt prism.

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**RESULTS AND DISCUSSION**

Crystalline KNCS falls in space group \( V h \).² There are four molecules per unit cell and the thiocyanate groups lie on sites of symmetry \( C \). The following correlation table relates the representations for the isolated ion, the site group, and the space group (see Table I). As mentioned in reference ¹ the NCS ions are arranged in parallel planes. These planes are perpendicular to the \( b \) axis. On the basis of the site group symmetry we should expect four fundamental infrared peaks: three of symmetry \( A' \), polarized perpendicular to the \( b \) axis and one of symmetry \( A'' \), polarized parallel to the \( b \) axis. Any combination band having an odd number of \( A'' \) vibrations should be polarized parallel to the \( b \) axis, while any combination band having an even num-

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**Table I. Correlation table for KNCS.**

<table>
<thead>
<tr>
<th>ISOLATED ION</th>
<th>SITE GROUP: ( C )</th>
<th>SPACE GROUP: ( V h )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>( \Sigma )</td>
<td>( A' )</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>( \Pi )</td>
<td>( A'' )</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td></td>
<td>( B_{1g} )</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td></td>
<td>( B_{2g} )</td>
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<tr>
<td>( \nu_5 )</td>
<td></td>
<td>( B_{3g} )</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td></td>
<td>( B_{4g} )</td>
</tr>
</tbody>
</table>

⁴ Reference ¹, Fig. 4.