Microscopic Crystallographic Description of Resublimed Chloranilic Acid

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Chloranilic acid was found to sublime rather than melt as reported in the literature. The sublimed and unsublimed materials were found to have identical spectra, which are given here from the ultraviolet through the visible to the infrared. The platy crystals which first formed in sublimed material later changed to acicular form. The optical and crystallographic descriptions of the crystals are given. Though the melting point of chloranilic acid is reported to be 283° ± 4° C., it sublimed at 240° C. at atmospheric pressure.

THE SUBLIMATION was readily achieved by heating the chloranilic acid in an evaporating dish using a cold watch glass as a cover. The sublimed chloranilic acid adhered to the watch glass in the form of needle-like crystals. The sublimation temperature of 240° C. was observed at 1 atm. of pressure using a block-type melting point apparatus. The first appearance of sublimed material is taken as the sublimation temperature. The absence of a melting point was demonstrated by heating the acid in a totally submerged sealed capillary at a rate of about 3 to 5 degrees per minute beginning at 25° C. using a Thiele-Dennis melting point tube. The recrystallized acid was placed in the sealed capillary tube and heated slowly to 305° C. No liquid phase was observed. When the capillary was cooled, the powdered material had not fused. A good portion of the crystals do decompose if they are heated rapidly or if heated over 300° C.

The crystals obtained by sublimation were orange to red in color, random in size, and had a characteristic needle shape. The chemical composition of these crystals was confirmed by determining the acid and chloride equivalent weights (Table I). The extinction coefficients and absorption spectra at different values of pH and ionic strength are identical to those of the recrystallized material (*2*)—see Table II and Figures 1 and 2. The concentrations of the acid are indicated on Figure 1.

Table I. Chemical Analysis

	Equivalent Weight	
Chloranilic Acid	Acid	Chloride
Fisher Reagent	105.5	101.3
Sublimed	104.5	102.8
Theoretical	104.49	104.49

Agreement between the molar extinction coefficient values of sublimed and recrystallized chloranilic acid show that the materials are identical (Table II). Visible and ultraviolet spectra (Figure 1) and infrared spectra of these two materials (Figure 2), as well as acid and per cent chlorine values (Table I) also show that the materials are identical. The microscopic examination of the crystals reveal the presence of two distinct crystalline forms as shown in Figures 3 and 4.

OPTICS

The optical properties of the crystals were determined with a petrographic microscope. The flat stage was used for general observation, determination of indices of refraction, and pleochroism. A universal rotating stage was mounted on the microscope for determination of the orientation of the indicatrix and estimating angles between crystal faces. Indices of refraction were determined by immersion in liquids of known index of Shillaber's set. The α and β indices were determined with liquids of 0.004 index spacing but γ was determined with liquids of 0.01 index spacings. The best values after temperature correction are:

$$\alpha = 1.566 \pm 0.002$$
$$\beta = 1.648 \pm 0.002$$
$$\gamma = 1.73 \pm 0.006$$

Pleochroism of the crystals is very marked in shades of brown. The X and Y vibrations directions show very similar absorption with both colors a moderate brown. The absorption in the X vibration direction is somewhat less than Y giving only a slightly lighter shade. Absorption is much greater in the Z vibration direction yielding a dark red brown color.

The crystals are clearly monoclinic both geometrically and on the basis of optical orientation. They are optically

Table II. Extinction Coefficients of Chloranilic Acid

	Concn.	For Sublimed Material			For Recrystallized Material		
Curve	*M*	215 mμ	325 mμ	535 mμ	215 mμ	325 mμ	535 mμ
0	0	...	...	...	...	...	...
1	2.2×10^{-5}	1.41×10^{4}	1.82×10^{4}	...	1.50×10^{4}	1.86×10^{4}	...
2	4.4×10^{-5}	1.43×10^{4}	1.82×10^{4}	...	1.45×10^{4}	1.86×10^{4}	...
3	5.6×10^{-4}	...	...	3.4×10^{2}	...	...	3.6×10^{2}
4	1.1×10^{-3}	...	...	4.3×10^{2}	...	...	4.4×10^{2}

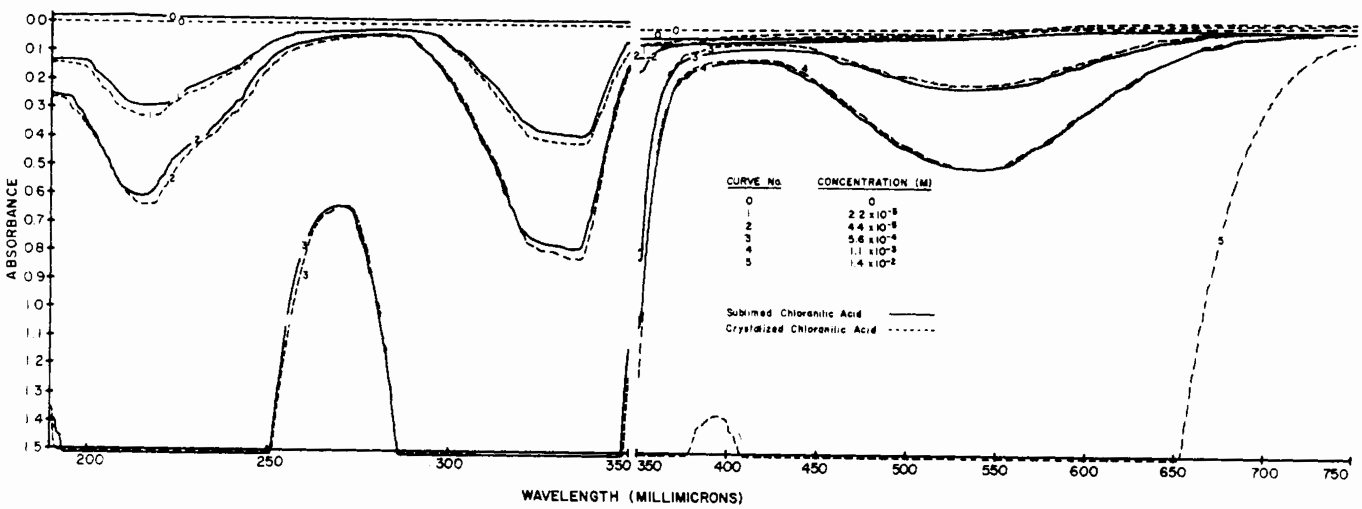

Figure 1. Superimposed ultraviolet and superimposed visible spectra of sublimed and of crystallized chloranilic acid

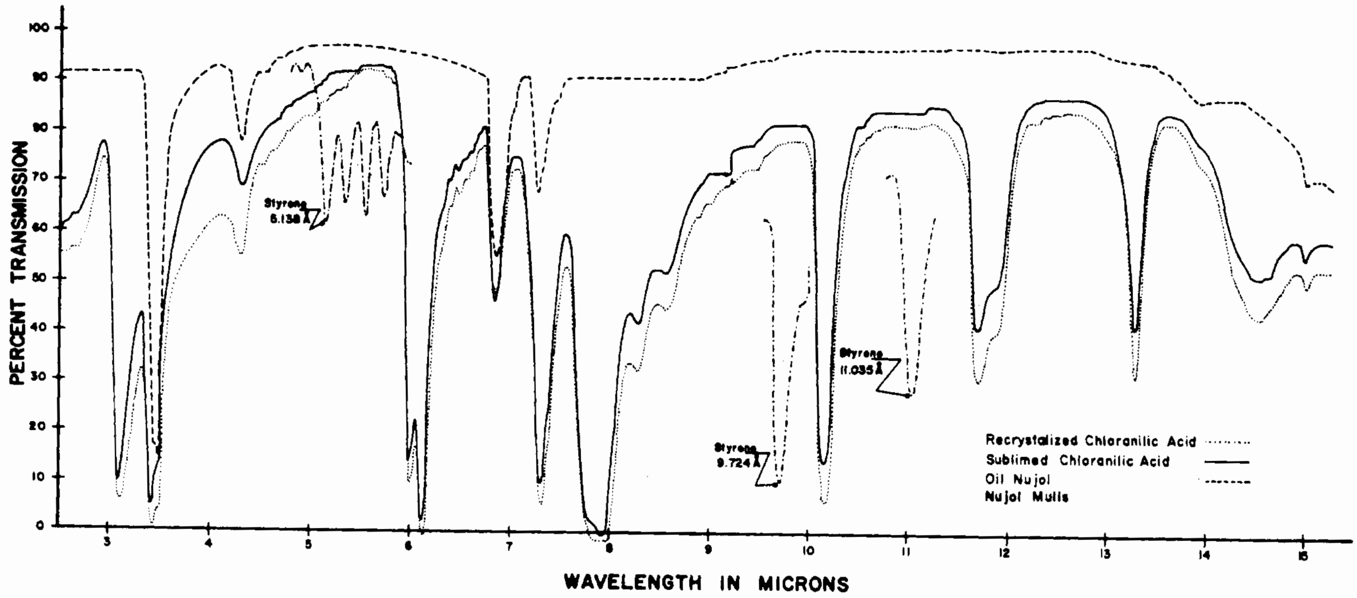

Figure 2. Superimposed infrared spectra of sublimed and of recrystallized chloranilic acid

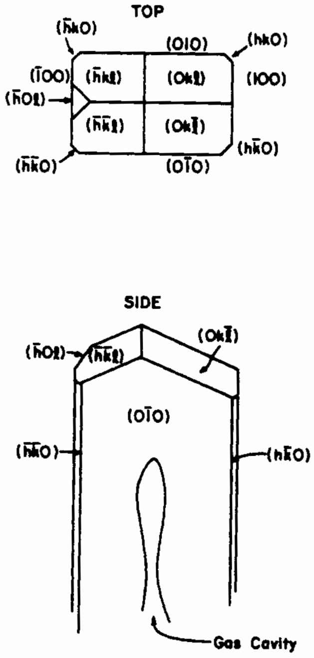

Figure 3. Acicular crystals

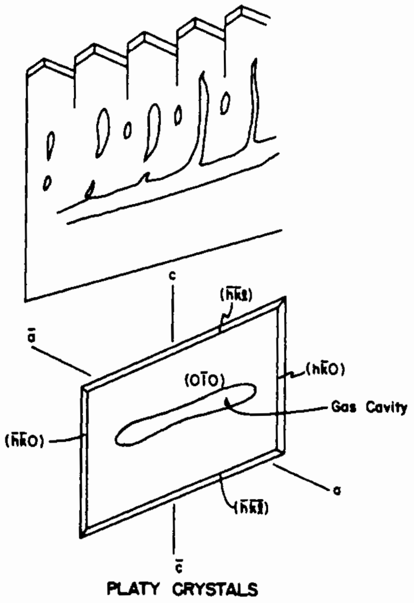

Figure 4. Platy crystals showing development of acicular crystals

biaxial positive with the interaxial angle, $2V$, approximately 60°. This angle was measured on the four-axis universal rotating stage. Chromatic dispersion of the crystals is weak with $2V$ for the red wave lengths greater than $2V$ for violet. In addition, the horizontal-type dispersion of the principal optic plane was recognizable, indicating that the obtuse bisectrix coincides with the b crystallographic axis. This agrees with the indicatrix orientation determined on the universal stage as follows:

$X = b$ crystallographic axis and the angle between Y and c crystallographic axis of $-2°$.

Two distinct habits of crystals are present in the sublimed material. One type is acicular and elongated on the c crystallographic axis. The other type is tabular parallel to the (010) pinicoid. The acicular crystals were studied first and optical properties were determined on them. Optical properties were checked later on the tabular crystals and were identical. The geometrical crystallography was worked out first on the acicular crystals, and then the tabular crystals were made to fit this geometry when the relationship between the two was recognized. No x-ray determinations were made.

The acicular crystals are dominated by the $a(100)$ and $b(010)$ pinicoids with a minor development of a third order prism, probably (110). The needles are terminated by two prisms, the larger of which was assigned as the first order prism $(0kl)$. The smaller then became a negative fourth order prism $(\bar{h}kl)$. In no crystal observed were both ends terminated so that the symmetry is either $2/m$ or m. The angle β between the a and c axes, as defined by the assigned first order prism, is approximately 115°. A very small negative second order $(\bar{h}0l)$pinicoid is present on some crystals. Many of the acicular crystals contain elongated gas cavities along the c crystallographic axis. Figure 3 is a sketch of these crystals and does not attempt to show interfacial angles closer than a few degrees. Stellate clusters of these crystals are common.

The tabular crystals are up to a millimeter in maximum dimensions but are very thin. They are dominated by the b pinicoid (010) with the edges truncated by a thin third order prism $(hk0)$ and a thin negative fourth order prism $(\bar{h}kl)$. Rounded elongated gas cavities are common in these plates with their long dimensions parallel to the negative fourth order prism zone. In some crystals, a transition from the tabular habit to the acicular habit can be seen by extension of growth along the c axis and the development of terminations identical to those of single acicular crystals. The $\bar{h}kl$ and $\overline{hk}l$ faces of the plate are then replaced with a saw-toothed edge as shown in Figure 4. In this growth process, the central gas cavity of the tabular crystals branches up the c crystallographic axis of each crystal.

REFERENCES

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Properties of Constant-Boiling Hydrochloric Acid–Zirconyl Chloride Solutions

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No data were available on the effect of dissolved zirconyl chloride on the constant-boiling hydrochloric acid–water azeotrope. Therefore, measurements were made (at atmospheric pressure) of boiling points, incipient crystallization temperatures, densities, and chloride concentrations in boiling HCl–H_2O–$0.2M$ to $3.5M$ $ZrOCl_2$. A decreasing HCl content with increasing $ZrOCl_2$ content maintained a nearly constant boiling point at about 111° C. Incipient crystallization temperatures increased from 41° to 95° C. with increasing $ZrOCl_2$ content.

BECAUSE data were needed on the effect of dissolved zirconyl chloride on the constant-boiling hydrochloric acid–water azeotrope, boiling points, incipient crystallization temperatures, densities, and chloride concentrations were measured at atmospheric pressure.

MATERIALS

Zirconyl chloride octahydrate was purchased from A. D. Mackay Co. The major impurities revealed by spectroscopic analyses were Si less than 50 p.p.m., Ca 10 p.p.m., and smaller amounts of Mg, Fe, and Cu. Reagent grade hydrochloric acid and distilled water were used to prepare solutions.

EXPERIMENTAL PROCEDURE

Zirconyl chloride–hydrochloric acid solutions were prepared by mixing $ZrOCl_2 \cdot 8H_2O$ with $9N$ HCl. Hydrochloric acid was distilled off at atmospheric pressure, using a single-plate distillation flask with a downdraft condenser. Distillation was continued until the volume in the distillation flask had decreased to the desired level. The boiling point was then monitored during a period in which the heating rate was decreased and the system approached total reflux. In no case was a change in boiling point detected during the last 10 minutes of this period. The 27 boiling points reported are those obtained as the system approached total reflux. Therefore, these boiling points may be considered to be the boiling points of constant-boiling HCl solutions containing specific concentrations of a third component, $ZrOCl_2$. It was necessary to determine boiling points in this way (by approaching total reflux during each determination) because the nonequilibrium conditions

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