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Newark, New Jersey
September 6, 1967

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EXAMINATION OF X-RAY DIFFRACTION RECORDS OF 4,11-Cl_2DQA

Preface

The products from which these x-ray records were derived were obtained by P. H. Griswold in a variety of different ways. The records were submitted to the writer for examination in the attempt to conclusively establish the existence of more than one crystal phase. This report makes pertinent observations on each of the series of x-ray patterns examined, but unfortunately, clear-cut evidence with regard to a multiphase system could not be established by simple inspection of the x-ray records.

Conclusion

4,11-Cl_2DQA very likely does exist in more than one crystal phase. The unstable α-phase is so unstable that it is difficult to obtain in a pure phase state. If two other more stable phases exist, they are at a considerably lower energy level than the α-phase and have energies so nearly alike that they too are difficult to obtain as a single phase species. These statements are based on a possible interpretation of the x-ray data, but cannot be considered unequivocal. More work must be done both from the point of view of sample preparation and also careful control in obtaining x-ray diffraction records before these statements can be verified.

Observations from the following Series

Series 5107-64 and 5107-68A (Dowtherm Reflux)

1. Acid crystallizing and hydrolyzing yields a poorly crystalline product. If a multiphase system is possible, this product should contain at least some of the unstable α-phase.

2. Refluxing in Dowtherm greatly increases crystallinity. The 15.5° peak is gone. The 13.6°, 14.0° doublet is well resolved. One would not expect much, if any, of the unstable phase in this product. It could consist of two phases of nearly the same stability.

3. Increasing the Dowtherm reflux to 5 hours yields a record much the same as that of 1 hour.

Series 5107-68B (DMF Reflux)

1. One hour DMF reflux shows a large increase in crystallinity. The 13.6°, 14.0° doublet is well resolved but the 14° peak is higher than the 13.6° peak. There is also a faint indication of the 15.5° peak as well as the 16° peak.

2. The 2 hour reflux is much like the 1 hour but the faint 15.5° peak is even fainter. Again the 14° peak is higher than the 13.6° peak. The relative intensity of these two peaks varies considerably from series to series and in many patterns it is the other way around. Sometimes the 14° peak is absent altogether. This could be used as evidence that one member of this doublet is due to one of the more stable phases and the other is due to another stable phase. However, another possible explanation is that the change in relative intensity is due to variation in crystal orientation in the x-ray mount.

3. The 5 hr. DMF reflux seems to show a regression to the 1 hr. sample. The 13.6°, 14.0° doublet has peaks of about equal intensity and the faint 15.5° peak is more prominent than at 2 hrs. The 16° peak is less prominent than at 2 hrs. Could this be due to orientation and if the same sample were run under different mounting conditions, would we see the same kind of variation between the 1 hr., 2 hrs., and 5 hrs. samples?

Series 5107-104 and 110 (Acid Paste to 40%)

1. Acid pasting (40% acid) does not give the poorly crystalline pattern that ordinary acid pasting and hydrolysis gives. The 40% acid shows the 16° peak and no 15.5° peak. The 13.6°, 14.0° doublet is resolved but the 13.6° peak is quite a bit more intense than the 14.0° peak. Refluxing in dimethylsulfoxide increases degree of crystallinity but the 14.0° peak of the doublet is almost gone. Also, the 20.4° peak is quite a bit more intense relative to the 19.9° peak after DMS reflux. This again suggests that there is a phase associated with a singlet at 13.6° (no 14° peak) and a peak at 20.4°, and another phase associated with a peak at 14° and 19.9°. An alternate suggestion is that the other phase is associated with a doublet at 13.8° and 41.0° and a doublet at 19.9° and 20.4°.

Series 5107-118-120; Very Dilute Pyrolysis in Dowtherm A or TMS

1. This yields very highly crystalline products. The 13.7° peak stands alone (no doublet - 14.0°). The 20.5° peak stands alone (no doublet - 19.9°). There is no 16° peak.

2. Even at high amplification, the x-ray record shows no evidence of the missing peaks.

3. However, mild mortar grinding shows the development of the missing 14° and 19.9° peaks. If orientation is responsible for the absence of these peaks, why does high amplification show no evidence of them? It is hard to believe that the orientation could be that complete. Does even mild grinding cause some phase conversion?

Series 5107-124; Acid Pasting (4%)

1. Acid pasting (4% H_2SO_4) yields a product similar to ordinary acid pasting/hydrolyzing. The product is rather poorly crystalline. It shows the 13.5°, 14.0° doublet and the 15.5° peak.

2. Ageing in the 4% acid environment increases the degree of crystallinity. If indeed an α-phase exists, this series illustrates it better than any of the other series examined, but it probably does not represent a single phase species. The doublet 13.6°, 14.0° is well resolved. The 15.5° peak is present. There is no 16° peak. There is a 19.9° peak.

3. This 124 series is confusing, however, in that simple heating in 4% acid caused some phase conversion if indeed we can call it phase conversion (124C) whereas refluxing in HOA^C (124D) did not. Could C and D be reversed?

Series 5107-160; Alcoholic KOH Pasting

1. The hydrolysis product from alcoholic KOH is very poorly crystalline. It probably contains α and something more stable. There is some slight evidence of a 15.5° peak. After HOA^C reflux, the stable phase or phases predominate and continuing the reflux simply increases the degree of crystallinity.

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