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Techniques. Hypodermic needles of gauge 27, the smallest available, were tried for extrusion of samples as described in the last report. They make samples 0.22 mm. in diameter as compared with 0.35 mm. for the ones previously used. However, it is not possible to make samples as long and 0.7 or 0.8 mm. appears to be the limit without clogging the tube. They could hardly be placed in the center of the x-ray beam without getting the supporting wire in the rays also. They would require two to three times as great an exposure and so far have not been used as there has been no need for better resolving power than that obtained with the larger samples.

Powder pictures. Vacuum pictures have been made of the Rumford sample (oxygenated) in the 7.5 and 15 cm. radius cameras. These show no large spacing ring such as appears on the Fankuchen pictures. However, these and other pictures described below show that the intensity of the "impurity" rings decreases as the sample becomes deoxygenated in vacuum. It is thus possible that the large spacing can be observed only for a fully oxygenated sample photographed in 15 cm. of oxygen. Pressure control is not at present available for the large cameras.

Attempts were made to obtain pictures of samples at equilibrium containing various quantities of oxygen. It is hoped that the samples could be held at a definite pressure of oxygen till equilibrium was reached, as shown by no further change in the x-ray pictures, and that the oxygen content could be estimated from the pressure-composition curve.

The U. of C. oxygenated sample was photographed under 14 cm. of oxygen. In previous reports this sample was said not to show the "impurity" lines which are quite strong for the Rumford sample. In the absence of scattering

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from nitrogen the pictures are much clearer in the larger spacing region and these two lines can now be seen for the U. of C. sample but their intensities are not comparable with those from the Rumford sample. After holding the sample at 8 cm. of oxygen for 8 hours a 14 hour exposure was made. Then, still maintaining the 8 cm. pressure, a 25 hour exposure was made. Although the total time at 8 cm. was 47 hours these pictures are identical with the first one, made at 14 cm. In this time some oxygen must have been lost but perhaps not nearly half, as required by the pressure-composition curve. The oxygen pressure was then reduced to 6.4 cm. and after 4 hours an exposure of 18 hours was made. During this exposure the pressure dropped to 5.1 cm. due to a leak through the pressure valve into the pumping system. The total time at reduced pressure was now 69 hours but the last picture is still indistinguishable from the earlier ones. The pressure was then reduced to the vacuum of the mechanical oil pump and after standing 7 hours two exposures were made, 19 and 20 hours respectively. These two are identical and are the deoxygenated pattern with no certain line of the oxygenated pattern visible. The second "impurity" line of d = 3.93 Å has faded out, as mentioned above, and is nearly invisible. The one of d = 6.74 Å appears unchanged. Pure oxygen was then added to atmospheric pressure. After one day pressure was reduced to 14 cm. and an 18 hour exposure made. This is again the oxygenated pattern. The "impurity" line of d = 3.93 Å is back at least to its former intensity.

These observations cannot be interpreted with certainty because equilibrium probably was not established even after the long times involved. This was not realized at the time. It is planned to repeat the experiment using weighable quantities of material in the pressure controlled chamber.

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When the weight ceases to change x-ray samples can be taken and photographed at the equilibrium pressure.

The results do suggest that the so-called impurity is another active compound. They also support the view that there is no gradual change in lattice constants but a sharp break in structure. This is not incompatible with the sigmoid type of pressure-composition curve obtained at Berkeley. It is not impossible that the oxygenated arrangement can maintain itself without its full quota of oxygen. As oxygen is removed holes are left in the otherwise undisturbed structure and the partial pressure of oxygen would fall. The x-ray patterns might not be visibly changed. All the oxygen of the fully oxygenated compound has a scattering power less than 5% of that of the rest of the structure. A considerable loss would not be detected if the structure holds together with insignificant changes in lattice constants. Examples of similar situations are well known. There would be some critical oxygen content below which the arrangement would be unstable and would change over to the oxygen-free structure. This in turn might have some holes in it which could accommodate with some strain some oxygen and account for the small amount of oxygen retained at very low pressures. It seems likely however that there might be a composition range in which the oxygen-free structure and the oxygenated structure of critical composition exist together.

Sublimed crystals. Three crystals selected from the batch brought back from Berkeley have proved to be inactive, apparently identical with the crystals from alcohol. Zero layer Weissenberg photographs about the $\underline{b}_o$ axis are identical (within the spacing accuracy of the instrument) and the $\underline{b}_o$ repeats from oscillation photographs are the same. Indexing the layer lines leads to identical unit cells. The intensities of spots which have been observed for both kinds of crystal are the same, within the errors of visual estimation.

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Yet there is a curious and baffling difference in the dichroism. The crystals from alcohol, either tabular or needlelike (see report for June) when lying on their {001} face show slight dichroism but are definitely darker with the electric vector perpendicular to $\underline{b}_o$ (the needle axis). The sublimed needles seem more strongly dichroic when lying on the same face and are darker, almost black, with the electric vector parallel to $\underline{b}_o$. One can hardly believe that crystals with such different optical properties are the same. Yet from the x-ray results to date they are the same. The only explanation that has so far come to mind is the following. In the usual formula written for salcomine the two unsaturated groups are isolated from each other by the carbon-carbon single bond of the ethylene group. If in the sublimation two hydrogens split off, thus producing a double bond at this point, the two unsaturated groups would no longer be isolated and the possibility of electrons getting from one to the other might effect the optical properties of the molecule greatly. But the overall shape of the molecule would be practically unchanged and they might pack together to form the same structure as unmodified molecules. The loss of two electrons would hardly be detectable by x-ray examination. There might be slight differences in lattice constants too small to detect at small scattering angles. This possibility will be investigated. In the meantime it would be well if the difference in optical properties can be substantiated elsewhere. It would also be interesting to recrystallize sublimed material from alcohol. We do not have a large enough supply here to make the experiment, particularly as it is hoped that further investigation of the sublimed material will discover single crystals of active material.

Since it has seemed desirable to determine the approximate crystal structures of the active and inactive materials to see if they explain the cause of the activity, complete sets of pictures are being made of the inactive

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crystals now mounted. These are nearly finished. From them it has appeared desirable to select a new $\underline{c}_o$ axis. The new cell has $\underline{a}_o$ = 14.08 Å, $\underline{b}_o$ = 7.03 Å, $\underline{c}_o$ = 26.20 Å and $\beta = 97°45'$. The length of $\underline{c}_o$ has not yet been confirmed by an oscillation picture but appears quite certain. If this cell is confirmed the systematic extinctions are hkl when k+l is odd and h0l when h or l is odd. These indicate space groups Aa or A2/a and the x-ray results cannot distinguish between them. There can be either four or eight molecules per cell according to space group requirements. If there are eight the calculated density is 1.67 gm./cc., a reasonable figure. Four would give a density much too low and other higher numbers would be impossibly high. If A2/a is the correct space group the molecules, even though they possess a two-fold axis, cannot be located on the two-fold axes of the space group because there are only four of the latter and the $\underline{b}_o$ repeat is too small to accommodate two molecules per axis. The molecules would thus be in general positions with 63 parameters to be fixed to determine the structure. If Aa is correct the situation is even worse. There would then have to be two crystallographically non-equivalent molecules per cell and 126 parameters. The most complicated structures previously worked out anywhere involved about 60 parameters. But it may still be possible to determine fairly easily the positions of the cobalts and the general orientation of the organic part of the molecule. Magnetic anisotropy measurements would probably be of great assistance if they could be obtained.

Pasadena, California
September 8, 1942

Signed Edward W. Hughes
Edward W. Hughes

2 cc to Calvin
1 cc to Pauling
1 cc to Hughes

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