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TECHNIQUES. It has been found that W. and M. gauge No. 32 steel wire of diameter .0128" fits the No. 23 gauge hypodermic needle bore even more closely than the No. 28 B. and S. gauge chromel wires previously used. The clearance is probably less than .0005", and the wires, after cutting, must be carefully polished with rouge paper to remove the burs formed by cutting. Since this wire is also much stiffer than chromel greater forces may be used without danger of bending and so longer and more tightly packed samples can be extruded.

SINGLE CRYSTALS. A considerable number of the last batch of sublimed crystals from Berkeley have been examined under the microscope. They have proved without exception to be very badly twinned. This may be because they grew rather suddenly towards the end of a run after it had been thought that the attempt to grow crystals had failed. Moreover, from their optical behavior and general appearance it is almost certain that a large number of them are the inactive form. For instance, the dichroism is that of the inactive form as from alcohol, darker with the electric vector perpendicular to the needle axis. Some however appear to be active but these are the ones most badly twinned and there are no single pieces separable large enough for photographing.

Although active single crystal pictures are not yet available a start has been made on a more detailed interpretation of the pictures completed some time ago of the inactive form. This work is continuing at present.

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POWDER PICTURES OF DIAMINES AND TRIAMINES. It was found impracticable to obtain good powder pictures of the coarse grained samples by grinding and sieving. The finest sieves available, about 325 mesh, are still too coarse for stationary samples. It so happened that the samples involved were all either inactive diamines or were triamines active only at high oxygen pressures. Consequently they were all photographed using the regular 5 cm. radius open camera which permits oscillation of the sample about its axis. These pictures completed the series.

In computing the results the following possible corrections were considered. It was ascertained, by means of marks made upon the films with two sharp steel pins set in a heavy brass rod, that the film used does not shrink or expand permanently during processing by an amount significant in this work. Consequently a correction for such an effect was ignored. Similar tests revealed however that the film contracted due to dehydration in the vacuum camera and on comparison with the length after processing it was found necessary to apply a small correction, which comes to about 0.4%, to films exposed in vacuum.

The resulting ring diameters from all films have been multiplied by factors which convert them to 5 cm. radius data. The radius correction factor for the 5 cm. camera was determined with a sodium chloride picture. The radius of the small vacuum camera was fixed by pairs of pictures from this series of the same sample made in both cameras. The spacings were then read off a large scale curve sheet showing spacing against ring diameter for Co K radiation (= 1.787 Å) and camera radius = 5.00 cm. The results are least certain for the small camera (d = 2.86 cm.) but are reliable probably to 0.5% and certainly to 1.0%. Smaller spacings are more certain than larger ones. The results are tabulated to show ring diameters as measured, and as corrected to 5 cm. radius, and also to show corresponding spacings. The measured diameters

1262639

CONFIDENTIAL

are convenient for identification work with our cameras. The additional values would be needed for work elsewhere and will be supplied upon request. Visual estimates of intensities have also been recorded.

Some general observations concerning these pictures have already been made in a previous report.

It appears likely that the sample of Co-o-hydroxy-acetophenone-en is a mixture. Some rings are spotty, indicating large crystallites, while others are quite smooth, indicating much smaller crystallites. The two quite different size ranges must necessarily belong to different substances, although they may be two forms of the same molecular species. The pictures of Co-3-nitro-sal-en also show two weak small spacing rings of very coarse structure which indicate the presence of a small amount of coarse grained impurity. On the other hand, the fact that the remaining pictures show all rings appearing the same does not guarantee the purity of these other samples.

Upon comparing the pictures of the seven active diamines it appears that one can make some generalizations.

They all show a strong to very intense line in the spacing range 9.9 Å to 14.0 Å and this spacing is practically unchanged during oxidation. But most, although not all, the other material materials show such a ring also and it appears likely that it is the spacing produced by stacking the planar molecules approximately end to end the long way. The length of the molecule without substituents in positions 4, 5, or 6 is about 11.0 Å and with allowance for packing differences the distances from cobalt to cobalt along the long way of the molecules would be in the range specified. Such distances should not be greatly influenced by oxidation of the active forms.

1262640

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The active oxygen-free forms also all show either one or two strong lines in the range 3.50 Å to 3.20 Å. These rings without exception move inward, increasing in spacing, upon oxygenation. Where there are two the outermost generally fades out. For the four most active compounds, Co-sal-en, Co-3-F-sal-en, Co-3-MeO-sal-en and Co-3-EtO-sal-en, the change in appearance is very great. The spacing range for the remaining strong line of the oxygenated forms is only from 3.47 Å to 3.60 Å.

All other lines are much weaker than those mentioned above except for the parent compound and for the 3-F compound. These two resemble each other in many ways and each has one extra strong line, at 7.62 Å for the parent and at 8.15 Å for the 3-F. These lines decrease slightly in spacing on oxidation.

The spacings in the range 3.20 Å to 3.50 Å might very well be approximately the spacing between nearly parallel molecular planes for adjacent molecules. This is about the value observed for packing together of aromatic ring compounds. But it must be emphasized that the crystal plane spacing, which is what is observed, need not be exactly the spacing between the planes of the molecules. The latter need not, and in low symmetry crystals generally do not fall parallel to any crystallographic plane. In fact, adjacent molecules need not be exactly parallel to each other in complicated structures such as these.

The fact that the faster compounds show such great changes in pattern on oxidation while the others show only slight changes, suggests that in the first case a real phase change is involved and oxygen adds on at the phase boundaries. The slower compounds would involve no phase change but merely a gradual change in lattice constants as oxygen diffused into the structure and

1262641

CONFIDENTIAL

from all observations these changes are small. The diffusion would explain the low rates. The two phase character has of course been confirmed for the parent compound.

It should also be recalled from the previous report that Co-3-methyl-sal-en, which is reported inactive, yields a powder picture very similar to that from Co-3-MeO-sal-en, which is active and fairly fast. This observation seems to indicate that both the chemical structure of the molecule and the way in which the molecules can pack together into a crystal structure are important in determining activity. On the other hand it may be that the similarity between these two pictures is entirely fortuitous.

Co-3-Ethoxy-Sal-En. The pseudomorph pictures from the red hydrate have not as yet led to the indexing of the powder pictures. A faint ring appearing only on the powder picture of the peroxide derived from the red hydrate and which had been ascribed to an impurity, appears also on the pictures of a single pseudomorph. It is as well oriented as other pseudomorph rings and vanishes on deoxidation. The significance of all this is uncertain. If due to an impurity the latter must be in solid solution in the hydrate and on dehydration form crystallites of its own which are well oriented with respect to those of the rest of the psuedomorph.

Pasadena, California
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