

CHANGED TO Unclassified

CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA 4

BY AUTH. CG DAR-1 4.3.1

BY Don B. Am DATE 4/1/96  
BY H.E. Brundage ADD 3/15/94

GATES AND CRELLIN LABORATORIES OF CHEMISTRY

729957

June 10, 1943

R

Professor Melvin Calvin  
Department of Chemistry  
University of California  
Berkeley, California

~~CONFIDENTIAL~~

Dear Calvin:

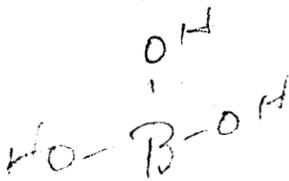
I am transmitting herewith the report for May. Besides the items mentioned I have also made additional efforts to index the powder pictures with no success to date.

After our conference I examined the 3-fluoro pictures and thought that our program could not be carried out as the active O-free compound seemed to show a weak ring at the same place as the strongest unique ring of the oxide. If so, this would prevent anything more than an approximate estimate of the first appearance of the oxide. This weak ring however is one of those mentioned in the report which do not appear on the pictures of material from the piperidinate. I shall now make test pictures with glass tubes and perhaps with Mo radiation. It probably would be a good thing if I had samples of any new active material you may have made, particularly of any that appeared particularly good.

If you have any guesses as to the identity of the substance that appears during cycling of the 3-fluoro and can send along samples I could easily make check pictures.

You may recall that in an early report I pointed out that the optical properties of the sublimed inactive salcomine were usually different from those of the crystals from alcohol, but that the x-ray patterns seemed to be identical. I worried some about what might cause this. It has just been called to my attention that a similar situation exists which is fairly well known although it too is not understood. During the last war ammonium picrate delivered to the Ordnance Department varied from yellow to orange in color but seemed otherwise identical. Investigation showed that crystals from water are yellow while those from strong ammonia water are orange. With the polarizing microscope the yellow form is seen to be slightly dichroic, being different shades of yellow for different positions of the electric vector. The orange form is very dichroic, being yellow at one position and red at the other. This is just about the kind of difference observed for inactive salcomine and in each case intermediate properties seem to be possible. I have made powder pictures of the two picrates and as nearly as I can tell they are identical.

I hope you have some luck with the sublimations. Incidentally, I feel quite certain that Fankuchen's crystals were not salcomine, but are



This document contains information affecting the National Defense of the United States within the meaning of the Espionage Act, USC 50c, and its transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

HBO  
OH  
B

1262501

Professor Melvin Calvin

-2-

June 10, 1943

very likely still another crystal form! His cell constants, which I have confirmed from his pictures, (which I have), will not index our powder pictures. But they show the characteristic intense  $13.0 \text{ \AA}$  spacing and its very peculiar orders which I mentioned in Berkeley.

Best wishes to all.

Sincerely,

*Edward W. Hughes*

Edward W. Hughes

Enclosures

**CONFIDENTIAL**

1262502

**CONFIDENTIAL**

NDRC-Chem-8

Monthly Report, May 1 - 31, 1943

Co-orthoacetyacetophenone-en. In a previous report it was stated that sample 5 of this material was probably impure. Since this sample had not exhibited full theoretical capacity a new sample was prepared at Berkeley. The new sample (Nos. 26 and 27) has now been photographed and the pictures are very different from the old ones. Sample 5 could not have contained more than about twenty per cent of the form in the new preparation, which is reported to have full capacity. It was also stated that sample 5 showed very little difference between its oxide and its oxygen-free form. This it now appears was because it contained so little active form. The new preparation yields pictures which resemble very strongly the corresponding pictures of the parent compound. The resemblance is particularly marked for the oxygen-free forms and persists in a general way to quite high scattering angles. The shifts of the stronger lines upon oxygenation are also very much the same.

Co-orthoaminobenzaldehyde-en. This substance differs from the parent only in the substitution of NH groups for the two oxygen atoms. It is inactive and the powder photograph is quite unlike those of any of the other diamines. There is the very intense inner ring of spacing about  $13.0 \text{ \AA}$  which occurs so frequently. And then, with the exception of one very faint ring there are no other spacings till one gets out to about  $5.0 \text{ \AA}$ , after which there are a lot of closely spaced rings of considerable intensity. It is likely that the unit cell is much longer in one direction than in the other two directions.

1262503

This document contains information affecting the National Defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794, and the transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

~~CONFIDENTIAL~~

Co-3-fluoro-sal-en and its hydrates. Samples of the two hydrates, one of which yields upon dehydration a fast active compound and the other of which yields a slower compound, have been photographed. The patterns are very different. The so-called "slow hydrate" is a coarse grained material yielding spotty rings which resemble somewhat in position and intensity those of the parent oxide. The "fast hydrate" is a finer grained material which yields nice smooth rings. The crystallites are smaller than  $10^{-3}$  cm. Both patterns show the intense  $13.0 \text{ \AA}$  spacing. Both samples appear to be pure to the extent that each does not contain a detectable amount of the other.

Desolvation of the piperidinate is reported occasionally to produce samples of low activity and one of these that is practically completely inactive has been investigated. The pattern is markedly different from that of the active form, and has also been detected in some deteriorated material. The evidence is therefore very good for a new inactive crystal form of this chelate. The  $13.0 \text{ \AA}$  ring is very weak compared to its usual intensity in other patterns and it may not really be a part of the inactive pattern. It may be due to a small amount of some impurity, probably the active form. This line would appear, if not interfered with, long before any other line of the impurity would show up.

The only active material previously photographed was prepared by dehydration of a sample which more recent work at Berkeley indicates was a mixture of the two hydrates described above. We now have pictures of the active form prepared from the piperidinate. These differ slightly from the former pictures, chiefly in that a few weak lines are now absent. At present it appears likely, although not certain, that the older active material from the mixed hydrate contains some impurity. Its identity cannot be determined from the powder pattern but it seems also to be present in the deteriorated samples described below.

1262504

**CONFIDENTIAL**

Pictures have been prepared from the samples taken from the life tests run at Berkeley. One sample was the active form from the piperidinate, mentioned above, after nearly 1500 cycles in dry air. The other was a similar sample derived from the "fast hydrate" after about 1600 cycles. Both materials were down to about 60% activity. These are the first samples of any deteriorated material to be examined by x-rays before deterioration had become almost complete. The two samples yield practically identical pictures. There is a good amount of the active material left and the pictures are chiefly those of the active form. However, one can detect easily three lines of the inactive form which are not interfered with by any lines of the active form. The identification is fairly certain and there may be as much as ten percent of this form present. In addition there are three other extraneous lines visible, one moderately strong at very large spacing. These agree in spacing and intensity with the lines which appear on the pictures of the old active material from the mixed hydrate but which do not appear on the pictures of the new active material from the piperidinate. As things stand at present, this supposed impurity which seems to form also during deterioration can be identified only by isolating it in pure form, checking its identity with a powder photograph, and making a chemical analysis.

Pasadena 4, California  
June 9, 1943

Signed Edward W. Hughes  
Edward W. Hughes

Approved Linus Pauling  
Linus Pauling

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

1262505