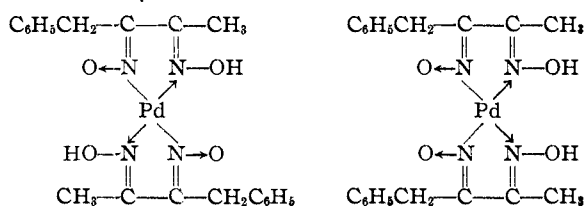


the one case examined it was found that palladium coordinates with two molecules of *anti*-diphenylglyoxime, and with one molecule only of each of the *amphi* and *syn* forms of the glyoxime. While further examples of the formation of four-covalent inner complex compounds with palladium and *anti*-glyoximes are required to make out a more satisfactory case, it seems reasonable to assume that it is the *anti*-benzylmethylglyoxime which is concerned in the formation of the yellow isomers. That the melting points of the glyoximes recovered from each of the isomers were the same as that of the original glyoxime is considered to be due to the extreme lability of the different forms of benzylmethylglyoxime which on heating give rise to an equilibrium mixture. Further, the fact that the glyoxime recovered from each isomer when added again to sodium chloropalladite produces a mixture of the two isomers but none of the compounds containing one molecule of the glyoxime indicates that only the *anti*-glyoxime is present in the isomers. Since coordination is effected through the two nitrogen atoms, palladium forms part of a five-membered ring with the *anti*-glyoxime, and the isomers may be formulated as follows:



The experimental justification for considering each molecule of a glyoxime as occupying two coordination positions has been discussed by Pfeiffer and Richarz.¹¹ It is improbable that isomerism is due to a *cis-trans* distribution of the hydrogen of the hydroxyl groups since a planar or pyramidal distribution of the glyoximes about the central palladium would give rise to eight isomers of the *cis-trans* type. Moreover, it is usually considered that mobility of this hydrogen would give rise to inseparable tautomeric mixtures.⁷ Nor does it seem at all probable that isomerism arises from the existence of both planar and tetrahedral configurations, since in this case four isomers should exist. There is, however, so far, nothing to indicate whether isomerism is due to a planar or pyramidal arrangement of the glyoxime about palladium. All attempts to prepare from the isomers derivatives suitable for possible resolution into optical antipodes have failed.

Summary

Two isomeric inner complex compounds of palladium with benzylmethylglyoxime have been prepared. Evidence is adduced to show that these substances are *cis* and *trans* isomers of palladium bis-*anti*-benzylmethylglyoxime.

(11) Pfeiffer and Richarz, *Ber.*, **61**, 103 (1928). See also Thilo, *Ref. 10*.

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Structural Changes Taking Place during the Aging of Freshly Formed Precipitates. IV. Aging of Fresh Lead Sulfate at Room Temperature in the Air-Dried State, and of Precipitates Covered with an Adsorbed Layer of Wool Violet

BY I. M. KOLTHOFF AND CHARLES ROSENBLUM

In the third paper of this series¹ it was shown that the speed of aging of fresh lead sulfate increases with the solubility in the liquid medium with which the precipitate is in contact. Since the fresh precipitate has a highly porous structure² the aging might be attributed to an internal recrystallization of the amicroscopic particles when the capillaries are filled with water or a dilute aqueous solution. In order to decide whether the

recrystallization takes place mainly by way of the external liquid or internally, we made the following investigation in which freshly precipitated lead sulfate was made air dry and then kept for shorter or longer times at various humidities. In addition, the speed of aging was investigated after adding wool violet to the suspension of the freshly formed lead sulfate. From previous studies³ we know that an adsorbed layer of wool violet pre-

(1) *THIS JOURNAL*, **57**, 597 (1935).

(2) *Ibid.*, **56**, (a) 1264, (b) 1658 (1934).

(3) I. M. Kolthoff, W. von Fischer and Chas. Rosenblum, *ibid.*, **56**, 832 (1934).

vents or strongly inhibits the recrystallization of aged lead sulfate. Therefore any aging found in the presence of the layer of adsorbed dye may be attributed to an internal recrystallization.

Aging of Lead Sulfate in Air-Dry State.—Fresh precipitates of lead sulfate were prepared in the air-dried state in a manner similar to the method described in the third paper of this series.¹ After sucking air with a relative humidity of 0.6 for fifteen to thirty minutes through the precipitates, which had been washed with alcohol, they still smelled faintly of alcohol.

Samples of these air-dry precipitates were placed in hygrometers of various humidities, and several portions were kept over pure ethanol. After a week of standing, the following experiments were made with the different samples.

1. The adsorption of thorium B was determined after fifteen minutes and three hours of shaking, respectively, with a radioactive lead solution containing 0.0016 mole of lead nitrate and 0.065 mole of potassium nitrate per liter. This solution is identical with that used in previous work.^{1,2} The weights of the samples of lead sulfate were determined at the conclusion of the experiments. By comparing the amounts of exchanged lead with those found with precipitates aged in the mother liquor,² it was possible to draw definite conclusions concerning the progress of the aging in the air-dry state.

2. The alcohol content was determined by a volumetric method. A weighed portion of the sample was treated in a cleaned iodine flask with 20 to 40 ml. of 0.05 *N* permanganate and 10 ml. of 4 *N* sulfuric acid. After standing overnight, the excess of permanganate was back-titrated according to the ordinary iodimetric method. The alcohol is quantitatively oxidized to acetic acid: $\text{CH}_3\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{H}_2\text{O}$. Blank experiments showed that the results were reliable to within 1 to 2% (relative).

3. The loss in weight was determined after heating to 100–105° to constant weight.

The results are reported in Table I. It is not claimed that the figures reported in columns 2 and 3 are accurate; the experiments should be repeated with larger samples taking more precautions against losses of water or alcohol during the weighing. However, it is evident that the samples kept over sulfuric acid and at a relative humidity of 0.6 contain only a trace of alcohol adsorbed.

TABLE I

AGING OF FRESH AIR-DRIED LEAD SULFATE AT ROOM TEMPERATURE (26°) FOR A WEEK AT VARIOUS HUMIDITIES

Rel. vapor press. water in hygromat	0	0.6	0.85 (25°)	Ethanol
Alc. content. mg./1 g. of lead sulfate	0.5	0.4	0.4	10.6
Loss in wt. at 110°, mg./1 g. of PbSO ₄	.3	.3	21.6	19.5
Lead exchanged, mg./1 g. of PbSO ₄ after shaking with Th B	15 min.	235	167	17.5
	3 hrs.	700	700	180
				700

Comparison of the amounts of lead exchanged with those found in previous studies² reveals that little, if any, aging takes place when the samples are kept at relative humidities of 0 to 0.6 for a week. After this time of aging the thorium B distributed itself throughout the entire precipitate after shaking for three hours. The samples kept at a relative humidity of 0.85 showed a distinct but slow aging. In addition it was found that these precipitates contained more than 2% of water. Thus the capillaries are filled with water; consequently an internal recrystallization may occur, although there is no external liquid present. This internal recrystallization, however, is much slower than that by way of the external solution. No aging was found when the air-dried samples were kept in an atmosphere of pure alcohol vapor, even though the capillaries were more or less completely filled with this solvent.

The thorium B experiments reported in Table I were repeated at ages varying between one and twenty-two days. Only the amounts of exchanged lead, found after fifteen minutes of shaking with thorium B, are given in Table II.

TABLE II

AGING OF FRESH LEAD SULFATE FOR DIFFERENT TIMES AT ROOM TEMPERATURE

Days of standing in desiccator	Lead exchanged in mg. per 1 g. of PbSO ₄ after 15 minutes shaking with Thorium B			
	Relative water vapor tension in desiccator			
	0	0.6	0.85	Ethanol
1	430	180	70	500
8	235	160	17.5	200
22	180	110	7.6	150

Evidently the aging over deliquescent sodium sulfate decahydrate progresses with increasing time of standing, but a very slight aging only occurs when the fresh precipitate is kept at relative humidities smaller than 0.6 or over pure ethanol over longer periods of time.

In this connection it was of interest to find out how the absorption of water by the precipitate changed on prolonged aging over deliquescent sodium sulfate decahydrate. If a distinct aging occurs when the fresh precipitate is kept at a relative humidity of 0.85, it may be expected that the amount of water absorbed would increase slowly with the time of standing until the capillaries are completely filled with water. On the other hand, as a result of the perfection process, the capillaries should gradually disappear and, on further aging, the amount of water absorbed should decrease. Therefore a distinct maximum

in the amount of water absorbed should be found after a certain time of standing over deliquescent sodium sulfate decahydrate. This was actually shown to be the case as is seen from the results reported in Table III. A fresh product of lead sulfate of slightly different age from that used in the experiments reported in Table II was prepared.

TABLE III

CHANGE IN WEIGHT OF SAMPLES KEPT AT A RELATIVE HUMIDITY OF 0.85 FOR VARIOUS PERIODS OF TIME

Standing, days	1	3	5	9	15	22
Increase in weight in %						
at R. H. of 0.85	0.45	0.80	1.1	1.3	1.8	2.2
Standing, days	26	32	42	54	70	
Increase in weight in %						
at R. H. of 0.85	2.3 ^a	2.0	1.2	0.45	0.3	

^a Maximum in amount of water absorbed.

Since a pronounced recrystallization occurs upon long times of standing at a relative humidity of 0.85, it might be expected that even the magnitude of the external surface of the lead sulfate would decrease upon long times of standing over deliquescent sodium sulfate decahydrate. The magnitude of the external surface expressed in mg. of lead per 1 g. of lead sulfate was computed from the maximum amount of wool violet adsorbed by the sample.³ From the results reported in Table IV it follows that the external surface hardly changes when the lead sulfate is kept at relative humidities smaller than 0.6 or over ethanol, but that a distinct decrease occurs when kept from forty to eighty days at a relative humidity of 0.85.

TABLE IV

CHANGE OF THE EXTERNAL SURFACE WHEN KEPT FOR FORTY TO EIGHTY DAYS AT VARYING HUMIDITIES AND OVER ETHANOL

Relative water vapor tension	0	0.6	0.85	EtOH
External surface ³ in mg. Pb per 1 g. PbSO ₄	2.2	2.5	1.5	2.4

Finally it may be added that the internal surface of freshly prepared lead sulfate which is in open communication with the exterior is reduced virtually to zero when the product is aged in the supernatant liquid for seventeen to twenty hours. Samples thus aged were collected, made air dry in the usual way, weighed and placed in a desiccator over deliquescent sodium sulfate decahydrate. The changes in weight were determined at regular intervals during a period of standing of two months. An initial increase in weight of less

than 0.035% was found, the weight remaining constant upon further standing. Thus, as a result of the aging in the mother liquor, practically all of the capillaries had disappeared and the products were no longer able to absorb water in the condensed state.

Aging of Lead Sulfate Covered with an Adsorbed Layer of Wool Violet 4 B. N.—To 10.30 ml. of 0.1 molar lead nitrate in paraffined containers was added 9.82 ml. of 0.1 *m* potassium sulfate and the suspension shaken for one, five and thirty minutes, respectively. Then 10.02 ml. of a dye solution containing 0.347 g. of wool violet per liter was added and the mixture shaken violently for one to two minutes. Without filtering, 9.94 ml. of a thorium B solution of the same composition (dye, lead nitrate and potassium sulfate) as the supernatant liquid was added. Again the containers were shaken violently for fifteen minutes and three hours, respectively, and the percentage of thorium B adsorbed determined.⁴ As usual all the experiments were carried out at least in duplicate.

In all of the six different cases it was found that $6 \pm 0.5\%$ of the thorium B was adsorbed, corresponding to 2.8 mg. of lead exchanged per 1 g. of lead sulfate. From these results it may be concluded that, although during the thirty minutes of shaking before addition of the dye a drastic aging had occurred, the magnitude of the external surface of the precipitate had not changed. After the precipitate has been covered with dye the thorium B cannot penetrate into the inside of the lead sulfate, since the same adsorption was found after fifteen minutes and three hours of shaking, respectively.

From these results it may be inferred that the external surface of *fresh* lead sulfate can be determined by the radioactive method if the precipitate is first covered with a layer of wool violet and then shaken with a thorium B solution for fifteen minutes or longer. According to this method the above precipitates possessed a specific external surface of 2.8 mg. of lead per 1 g. of lead sulfate, a result which is in close agreement with that derived from the amount of wool violet adsorbed.^{2a}

In connection with the problem dealt with in this paper we can draw the important conclusion from the above experiment that the adsorbed wool violet prevents the external recrystallization

(4) For experimental details see Ref. 3.

Had any recrystallization of this kind taken place, the amount of thorium B adsorbed would have increased continuously with the time of shaking, whereas actually the same adsorption was found after fifteen minutes and three hours, respectively, in the presence of the dye. An eventual *internal aging*, therefore, can be studied in the following way. To a fresh suspension of lead sulfate of known age enough wool violet solution is added to prevent external recrystallization. After various times of standing the precipitate is collected by filtration, the adsorbed dye removed, and the progress of the aging computed from the amounts of lead exchanged on shaking of the precipitates with radioactive lead solution for various times (see paper I^{2a}).

Great difficulty was encountered in the removal of the adsorbed dye. After standing in the dye solution for a given time, the precipitate was filtered and washed with water until the wash water was no longer colored. The lead sulfate, remaining strongly colored, was washed with 95% alcohol, 200 ml. being used altogether. The alcohol was then removed by sucking dry air through the precipitate for thirty minutes. Alcohol removed a large part of the adsorbed dye but, although the final washings were entirely colorless, the aspirated precipitate appeared to be distinctly blue. Part of this precipitate was used directly in exchange experiments with thorium B. The remainder of the precipitate, after the alcohol treatment, was washed quickly with five 2-ml. portions of 2 *N* nitric acid, then with 60–70 ml. of water, finally with 30 ml. of absolute alcohol and then aspirated for thirty-five minutes with dry air. Precipitates obtained in this way appeared to be colorless, or sometimes a trifle grayish, and therefore were better suited for the studies of the distribution of thorium B. A disadvantage of the procedure is that a drastic aging occurs when fresh precipitates are treated with nitric acid and with water. For this reason the washing process was carried out as quickly as possible.

In the following experiments the same precipitates were used as in the experiments described above (specific surface 2.8 mg. lead per 1 g.). After addition of the dye solution they remained in contact with the supernatant liquid for two days (forty-one hours), and then were filtered and washed according to the described procedures (with alcohol and with alcohol and nitric acid respectively). The air-dried precipitates were

then shaken for fifteen minutes and three hours, respectively, with a thorium B solution 0.0016 molar in lead nitrate and 0.065 molar in potassium nitrate.^{2a} The amounts of exchanged lead are reported in Table V. The last column gives the "apparent age." This figure represents the age of a precipitate which, when kept in the supernatant liquid without dye, would display the same values of lead exchanged after fifteen minutes and three hours of shaking with thorium B. These values were derived by interpolation from earlier experiments (papers I and II of this series^{2a,b}).

TABLE V
AGING OF FRESH LEAD SULFATE SUSPENDED IN WOOL
VIOLET SOLUTION FOR 2 DAYS (25–26°)

Precipitate washed with	Time of shaking with Th B	Pb exchanged in mg. per 1 g.	Apparent age
Alcohol	15 minutes	3.3 ± 0.2	48 hours
Alcohol	3 hours	5.1 ± .1	41 hours
Nitric acid	15 minutes	70 ± 10	26 minutes
Nitric acid	3 hours	220 ± 10	98 minutes

The results obtained with the alcohol washed precipitate are very misleading, since they would indicate that the speed of the aging process in the dye-coated precipitate suspended in the supernatant liquid is of the same order as without wool violet. Actually the small amount of dye left on the crystals after washing with alcohol was sufficient to inhibit further recrystallization and perfection as shown by shaking with the aqueous thorium B solution. However, after removal of all of the adsorbed dye by washing with nitric acid, it appeared that the dye-coated precipitate, although kept for two days in contact with the supernatant liquid, had aged very slightly if at all.

No more exact conclusions can be derived from these experiments since the washing with nitric acid promoted the recrystallization and perfection of the crystals.

In order to eliminate the effect of washing with nitric acid as much as possible, a new set of experiments was made. Dye was added to a freshly prepared suspension of lead sulfate, and the whole shaken for five minutes. After this period, half of the suspension was filtered through a Gooch crucible and the precipitate subjected to the washing process (water, alcohol, nitric acid, water, alcohol) as described above. The remaining half of the suspension was shaken for thirteen days, filtered, and the precipitate subjected to the same washing process.

TABLE VI
AGING OF FRESH LEAD SULFATE SUSPENDED IN WOOL
VIOLET SOLUTION

Time of aging in dye solution	Time of shaking with Thorium B	Pb exchanged in mg. per 1 g.	Apparent age in minutes
5 minutes	15 minutes	10.8	160
5 minutes	3 hours	108	160
13 days	15 minutes	10.2	210
13 days	3 hours	33	320

From the results obtained it may definitely be inferred that no external recrystallization occurs with dye-coated precipitates, but that a very slow internal perfection takes place, the speed of which is of the same order as that of air-dry precipitates kept over deliquescent sodium sulfate.

To verify the conclusions drawn from the above study, similar experiments were carried out with radioactive precipitates of lead sulfate.

For the sake of brevity the final results only are reported in Table VII.

TABLE VII
AGING OF FRESH, RADIOACTIVE LEAD SULFATE SUSPENDED IN WOOL VIOLET SOLUTION FOR FIFTEEN TO SIXTEEN HOURS (25-27°)

Precipitate washed with	Time of shaking with lead solution	Pb exchanged in mg. per 1 g. of PbSO ₄	Apparent age
Alcohol	15 minutes	1.50 ± 0.03	
Alcohol	3 hours	3.3 ± .1	
Nitric acid	15 minutes	10.5 ± 1	6.2 hours
Nitric acid	3 hours	28.5 ± 4	2.4 hours

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Discussion and Summary

1. The drastic aging of freshly prepared lead sulfate in its supernatant liquid is to be attributed mainly to a recrystallization by way of the

external solution. If the precipitate is coated with an adsorbed layer of wool violet, the speed of the above recrystallization is greatly inhibited, and hardly any aging is found even after shaking for thirteen days. The slight aging found is attributed to a slow recrystallization occurring in the inside of the precipitate.

2. Fresh and air-dried precipitates of lead sulfate, if kept at relative humidities of 0.6 or less, undergo hardly any aging upon long periods of standing. In addition they do not absorb water under these conditions. If kept, however, at a relative humidity of 0.85, a slow but distinct aging occurs, which is attributed to an internal recrystallization. Correspondingly it was found that under these conditions about 2% of water was absorbed in the capillaries of the precipitates. This water is slowly absorbed, and its amount reaches a maximum after a certain time of standing. Upon further aging the amount of water absorbed decreases as a result of the disappearance of the capillaries. When the fresh precipitate is kept over ethanol the capillaries are more or less completely filled with this solvent. However, no aging occurs on standing, since the speed of recrystallization of lead sulfate in ethanol is so much smaller than in water.

3. If freshly prepared lead sulfate is aged for seventeen hours in the supernatant liquid before being made air dry, it no longer absorbs water when kept at a relative humidity of 0.85. The capillaries have disappeared as a result of the perfection.

4. The external surface of fresh lead sulfate can be determined by the radioactive method if the precipitate is first covered with a layer of adsorbed wool violet and then shaken with a thorium B solution for fifteen minutes or longer.

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