[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Structural Changes Taking Place During the Aging of Freshly Formed Precipitates. VIII. Influence of Agitation upon the Aging and the Speed of Distribution of Thorium B

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In a preceding paper[1] the effect of the amount of precipitate and the concentration of lead ions in solution upon the speed of distribution of radioactive lead through fresh lead sulfate has been studied. In this paper the effect of the method and speed of agitating the suspension upon the speed of distribution is reported. Since both the speed of penetration of thorium B into fresh lead sulfate and the aging of the latter are attributed to a recrystallization of the precipitate, it was of interest to investigate whether the factors affecting the speed of distribution affect the speed of aging in a similar fashion. The results of such an investigation are described in this paper and throw new light upon the mechanism of the aging process.

Experimental

The batch of fresh lead sulfate employed was prepared and air-dried as previously reported. In all experiments on the radioactive lead solutions 0.3 g. of the product was shaken or stirred with 23.53 cc. of an active solution which was 0.00162 molar in lead nitrate and 0.065 molar in potassium nitrate. Details of manipulation are described in earlier papers.

Effect of Type and Speed of Agitation.—The following agitation devices were used: (1) standing (the suspension was not stirred or shaken, but only gently rotated two to three times to wet and disperse the lead sulfate); (2) rotation—end-over-end, 13 rotations per minute; (3) rotation on a horizontal plane, 128 rotations per minute; (4) high speed shaker—400 phases per minute (see THIS JOURNAL, **55**, 2656 (1933)); (5) motor driven glass stirrer, 1300 rotations per minute; (6) as 5, 400 rotations per minute; (7) as 5, 180 rotations per minute.

Three-tenths-gram samples were agitated for fifteen minutes only with the radioactive lead solution because the approximately 50% removal of thorium B which was found in this interval in most of the above cases permits the most accurate evaluation of the $Pb_{exchanged}$. The results recorded in Table I represent the average of several determinations.

TABLE I

EFFECT OF MANNER OF AGITATION UPON SPEED OF DISTRIBUTION OF ThB

15 minutes of agitation at room temperature

Method of agitation	1	2	3	4	5	6[a]	7[b]
ThB removed, %	11.9	51.1	44.6	50.2	47.6	43.7	26.5
$Pb_{exchanged}$, mg. p. 1 g. $PbSO_4$	3.8	29.3	22.6	28.3	25.4	21.7	10.1

[a] Slight settling of precipitate. [b] Much settling of precipitate.

As might be expected, hardly any penetration of thorium B occurred when the suspension was allowed to stand without agitation. It will be shown later in this paper that the precipitate under these conditions ages with the same speed as when the suspension is shaken violently. However, the thorium B in the above experiments is removed at the solid–liquid interface, where the introduction of fresh thorium B by diffusion from the solution is very slow if no stirring is applied. It is significant that the speed of agitation or of stirring is immaterial as long as the precipitate is prevented from settling. Thus in the experiments with the very slow end-over-end rotation (2), virtually the same thorium B removal was found as with the high speed shaking (4) or with rapid stirring (5). However, when the stirring is not efficient enough to keep all of the precipitate in suspension (7), the speed of distribution of the active lead diminishes markedly. Apparently rotation on a horizontal plane (3) is somewhat inefficient due to a slight centrifugal action.

Effect of Various Factors upon the Speed of Aging of Fresh Lead Sulfate

Effect of Varying Ratio of (Amount $Pb_{precipitate}$)/(Amount $Pb_{solution}$).—It has already been shown[1] that, the other conditions being the same, the speed of distribution of active lead decreases with decreasing amounts of suspended lead sulfate. It was found also that the speed of distribution decreases with increasing

(1) Kolthoff and Rosenblum, THIS JOURNAL, **58**, 116 (1936).

quantity of lead ions in solution, regardless of whether this quantity was varied by using more concentrated lead nitrate solutions or by taking larger volumes of a given solution. From the experiments reported below it will be seen that the speed of *aging* of lead sulfate is independent of the amount of precipitate and of the amount of lead in the solution, *leaving the concentration unchanged.* The speed of aging diminishes with increasing lead concentration in the solution, since the solubility and consequently the speed of recrystallization is decreased.

In the following experiments the indicated amount of fresh lead sulfate was shaken for one and one-half hours at high speed with a given volume of lead nitrate solution which was also 0.065 molar with respect to potassium nitrate. Then the precipitate was filtered, washed with conductivity water, absolute alcohol and made air-dry; three-tenths-gram samples of the air-dried products were weighed out and shaken for fifteen minutes and three hours in the high speed shaker (4) with a radioactive solution of the same composition as used in experiments reported in Table I. The amounts of lead exchanged were calculated in the ordinary way. The results are reported in Table II. For comparison 0.3-g. samples of the original product of lead sulfate were treated in a similar way. After fifteen minutes of shaking, the amount of $Pb_{exchanged}$ was found equal to 44 mg. and after three hours of shaking to 800 mg. per 1 g. of lead sulfate.

TABLE II

EFFECT OF AMOUNT OF PRECIPITATE AND OF LEAD IN SOLUTION UPON THE SPEED OF AGING OF LEAD SULFATE

Aging concn. of lead nitrate, M	Medium volume of lead nitrate, cc.	Amount of $PbSO_4$ during aging, g.	$Pb_{exchanged}$, mg. p. 1 g. $PbSO_4$ after shaking with ThB solution for 15 min.	3 hours
0.0162	25	3.600	10.3	60.5
.0162	25	1.244	9.4	54.0
.0162	25	0.310	9.0	58.9
.00162	25	1.244	6.2	22.0
.00162	250	1.245	4.1	16.0
.00162[a]	25	1.244	4.5	18.7

[a] Was not shaken during the aging period of one and one-half hours.

The last experiment (*a*) in Table II gives the results of experiments in which the lead sulfate was allowed to stand in the supernatant liquid without any agitation for the aging period of one and one-half hours.

These data show conclusively that the speed of aging of lead sulfate in a given supernatant liquid is independent of stirring, virtually the same age being found when the suspension was shaken violently during aging as when the mixture was allowed to stand undisturbed. Apparently the rapid aging is not to be attributed to an Ostwald ripening process, in which the smaller particles go into solution and the larger particles grow at the expense of smaller ones, since the speed of agitation would be of great consequence in the progress of such an aging. The above results suggest that the recrystallization, which is responsible for the aging and perfection, occurs with great speed in a liquid layer around the particles. Further work is planned to clear up the mechanism of this aging.

The results in this paper indicate that caution must be exercised in judging the speed of aging of fresh lead sulfate from the speed with which thorium B distributes itself through the precipitate. The conditions prevailing during the experiment must be considered before valid conclusions may be drawn.

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Summary

1. The speed of distribution of thorium B when a radioactive lead nitrate solution is shaken with a fresh precipitate of lead sulfate is independent of the speed of agitation as long as the precipitate is prevented from settling.

2. The speed of aging of fresh lead sulfate in a lead nitrate solution is independent of the amount of precipitate, of the amount of lead in the solution (the lead concentration being constant), and of stirring.

3. The recrystallization responsible for the drastic aging is not an Ostwald ripening process.

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