

a greater energy of desolvation, which appears in the higher energy of activation for the decomposition in water.

Summary

1. The decomposition of lithium and sodium trinitrobenzoates in ethyl alcohol has been found to be of the first order.

2. The decomposition of trinitrobenzoic acid in alcohol in the presence of aniline and substituted anilines has been found to be of the one-half order with respect to both acid and base when the ratio of acid to base is not too different from unity. This is the behavior to be expected if the decomposing substance is the trinitrobenzoate ion.

3. Choosing a suitable value for the equilibrium constant of the reaction between aniline and trinitrobenzoic acid, the initial rate of decomposition has been shown to vary directly with the calculated equilibrium concentration of trinitrobenzoate ion.

4. The variation of the rate of decomposition with the strength of the bases added to solutions of trinitrobenzoic acid in alcohol is in agreement with the predicted effect of the change in basic strength on the concentration of trinitrobenzoate ion.

5. The dissociation constant of trinitrobenzoic acid in alcohol has been estimated to be 1.7×10^{-4} .

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Studies on Aging of Precipitates. XXIV. The Apparent Effect of Filtration upon the Aging of Fresh Lead Sulfate. Aging of Lead Sulfate in Excess of Lead and of Sulfate

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In the present study the speed of aging of freshly precipitated lead sulfate was investigated in solutions containing an excess of lead nitrate or of potassium sulfate. In previous work² it has been found that the speed of penetration of thorium B into lead sulfate under standardized conditions is a good indicator of the progress of the aging of the precipitate and the method was applied to the present work. The samples of lead sulfate after aging were, as a rule, collected by filtration or centrifuging before they were shaken with the radioactive lead solution. The results obtained were very erratic and difficult to explain. It seemed that the method of collecting the precipitate had a great effect upon the speed of penetration of the thorium B. For this reason, the apparent effect of filtration upon the age of the lead sulfate was investigated in the first part of this study.

Apparent Effect of Filtration.—Lead sulfate was prepared by adding to a measured volume of

0.0665 *M* lead nitrate an equal volume of 0.0665 *M* potassium sulfate from a pipet in about twenty seconds (direct precipitation). In a few instances the precipitation was made in the reverse order (reverse precipitation). A precipitate in contact with the above supernatant liquid is called for convenience an "equivalent body." Most of the aging experiments in an excess of lead were made in what we call a "standard lead" solution. This was obtained by adding a lead nitrate solution to the suspension; the final solution was 1.59×10^{-3} *M* in lead nitrate and 0.0652 *M* in potassium nitrate. The experiments with thorium B were carried out in a solution of the same composition. Therefore, if the aging had taken place in the standard lead solution or as an equivalent body, a radioactive lead solution of suitable composition could be added to the suspension after aging without separating the precipitate from the mother liquor. After aging in excess of sulfate or in larger excesses of lead it was necessary to collect the precipitate; the latter was then suspended in a radioactive lead solution prepared by dissolving pure lead nitrate (c. p., thrice recrystallized) and c. p. potassium nitrate in conductivity water and then saturating with lead sulfate. This "syn-

(1) From the experimental work of a thesis submitted by William von Fischer to the Graduate School of the University of Minnesota in partial fulfillment of the requirements of Doctor of Philosophy, December, 1937.

(2) I. M. Kolthoff and Ch. Rosenblum, *THIS JOURNAL*, **56**, (a) 1264, (b) 1658 (1934); **57**, (c) 597, (d) 607, (e) 2373, (f) 2377 (1935); **58**, (g) 116, (h) 121 (1936).

thetic standard" solution was $1.59 \times 10^{-3} M$ in lead nitrate and $6.52 \times 10^{-2} M$ in potassium nitrate, and apparently was of the same composition as the above "standard" (supernatant) lead solution.

The pronounced effect of the method of collecting the precipitate upon the "apparent" age is shown clearly in Table I. The total age of the precipitates, shaken in the supernatant standard lead solution, was fifty-seven minutes when the thorium B was added.

TABLE I

EFFECT OF METHOD OF SEPARATION OF PRECIPITATE FROM MOTHER LIQUOR UPON APPARENT AGE

Speed of shaking with ThB, 400 cycles per minute; temperature 25° ; amount of $PbSO_4$ shaken with 30 ml. of ThB solution was 0.2 g.

Time of shaking with thorium B, hours	Product					
	A	B	C	D	E	F
0.25	33	10.8	10.0	14.5	18.7	35
1	139	20.6	27.4	33	113	220
3	476	31.7	50.5	99	339	499

- A. No separation between precipitate and mother liquor.
- B. Precipitate filtered after forty-five minutes through filter paper, etc.
- C. Precipitate filtered after forty-five minutes through glass crucible, etc.
- D. Precipitate centrifuged after forty-five minutes, (2200 r. p. m.), washed, etc.
- E. No separation between precipitate and mother liquor; after forty-five minutes a few shreds of filter paper were added, etc.
- F. No separation between precipitate and mother liquor; after forty minutes of aging centrifuged for five minutes at 2200 r. p. m.; finally shaken to age of fifty-seven minutes.

From experiment F it is evident that centrifuging alone has no effect. The striking effects reported in Table I, therefore, have to be attributed to a difference between the true and the synthetic standard lead solutions.

Actually, it was shown that a very slight coprecipitation of basic lead sulfate during the precipitation of the lead sulfate occurred. This coprecipitation is evident from the following pH measurements given in Table II. The pH was determined by means of the quinhydrone electrode at 25° . The pH of the "synthetic standard solution" prepared from pure materials was 5.42.

The supernatant liquid immediately after precipitation is distinctly acid, the pH being about the same in the cases of direct and reverse precipitation. In this respect the "true standard

TABLE II

pH OF SUPERNATANT LIQUID AFTER PRECIPITATION OF LEAD SULFATE AND AGING FOR VARIOUS PERIODS OF TIME

Age in hours	0	0.75	3	24
pH of liquid (direct ppt. standard lead)	4.12	4.55	4.94	4.98
pH of liquid (reverse ppt. standard sulfate) ^a	4.17	4.94	5.18	5.40

^a The supernatant liquid was $1.59 \times 10^{-3} M$ in potassium sulfate and $0.065 M$ in potassium nitrate.

solution" differs from the "synthetic" one. Upon aging in the supernatant liquid the pH increases indicating that the basic sulfate slowly reacts with the hydrogen ions in solution during the recrystallization process.

Subsequent experiments in which the aging and shaking with thorium B were carried out in media containing various amounts of nitric acid showed conclusively that *filtration* (avoiding shreds of filter paper) or *centrifuging* has no effect upon the aging of lead sulfate and that the huge apparent effect (see Table I) is caused entirely by the coprecipitated basic sulfate and consequently by the difference in pH between the supernatant and the synthetic standard lead solutions. The speed of recrystallization and, therefore, of aging of the precipitates containing basic sulfate in slightly acid solutions with a pH of 4 is very much greater than at a slightly larger pH of 5 (see Table I). The basic sulfate inhibits the speed of recrystallization; when the solution is slightly acid the contamination is removed during the perfection process and the latter can proceed at a reasonable velocity. When the pH of the solution is such that the basic sulfate is not extracted, the aging proceeds very slowly; when, on the other hand, the pH of the solution is small enough to allow a rapid extraction of the basic sulfate the aging will proceed much more rapidly than would be anticipated from the effect of the acid on the solubility of lead sulfate. The above results indicate very strongly that the coprecipitated basic salt is located mainly on the active surface of the highly imperfect precipitate. Previously, the large speed of recrystallization of a highly imperfect lead sulfate precipitate was attributed to a difference in solubility of lead sulfate on highly active and on more nearly normal surface. The presence of basic lead sulfate on active surface decreases the solubility, and, consequently, the speed of recrystallization is considerably lowered. In order to eliminate the effect of the coprecipi-

tated basic sulfate as much as possible, it is recommended in future work to determine the speed of penetration of thorium B in a medium containing a small amount of nitric acid (about 0.001 *N*).

Aging of Fresh Sulfate in Excess of Lead and of Sulfate

Speed of Perfection.—In previous work² it was not realized that the speed of penetration of thorium B from the "true" supernatant liquid into the precipitate was much greater than from the "synthetic" solution. For this reason some previous aging experiments in an excess of lead and of sulfate have been repeated and new experiments have been added. In all cases the effect of filtration has been eliminated.

Peculiar results were obtained after aging in 0.1 *M* potassium sulfate solutions. Even after long periods of aging, the precipitate, upon shaking with the radioactive lead solution, behaved as if it were extremely fresh. It was shown that these results were due to a transformation of the lead sulfate into a double salt $\text{PbSO}_4 \cdot \text{K}_2\text{SO}_4$. Randall and Shaw³ reported that lead sulfate is stable when the potassium sulfate concentration of the solution is smaller than 0.02245 *M*; at higher concentrations the sulfate is transformed into the double salt. When the latter is shaken with the radioactive lead solution the lead is quickly removed by reaction with sulfate, thus creating the impression that the precipitate is extremely fresh. Double salt formation probably also occurs during the "reverse precipitation." Hence, such a precipitate is not strictly comparable to that obtained by the "direct" method (addition of sulfate to the lead). In previous work^{2a} it was found that lead sulfate obtained by the reverse precipitation from 0.1 molar solution had a larger specific surface than a product obtained by direct precipitation. Moreover, the aging of the former, as indicated by the change in the amount of wool violet adsorbed, was more pronounced in a solution containing an excess of sulfate than in a solution containing the same excess of lead. In the present work, in which less imperfect precipitates were prepared from 0.0665 *M* solution, the same results were obtained.

The results of the studies of the speed of penetration of thorium B after aging under various conditions are given in Table III.

(3) M. Randall and D. L. Shaw, *THIS JOURNAL*, **57**, 427 (1935).

TABLE III

SPEED OF PENETRATION OF THORIUM B INTO LEAD SULFATE (DIRECT PPT.) AGED UNDER VARIOUS CONDITIONS (0.2 G. PbSO_4 ; 30 ML. OF TRUE STANDARD LEAD SOLUTION; TEMPERATURE 25°)

Aging medium	Age of PbSO_4 , min.	Mg. of lead exchanged per 1 g. after shaking for			
		15 min.	1 hr.	3 hours	
	Fresh	(980)	(730)	(700)	
Standard lead	12	221	(710)	(760)	
Standard lead	20	98	391	(850)	
Standard lead	45	57	317	606	
Saturated lead sulfate	45	35	110	610	
0.01 <i>M</i> $\text{Pb}(\text{NO}_3)_2$	45	140	438	640	
0.1 <i>M</i> $\text{Pb}(\text{NO}_3)_2$	45	310	(715)	(700)	
Standard sulfate	45	83	437	640	
0.01 <i>M</i> K_2SO_4	45	179	615	(800)	
Standard lead	180	9.2	37	128	
Saturated lead sulfate	180	7.5	13	75	
0.01 <i>M</i> $\text{Pb}(\text{NO}_3)_2$	180	49	295	540	
0.1 <i>M</i> $\text{Pb}(\text{NO}_3)_2$	180	295	610	(700)	
Standard sulfate	180	16	28	160	
0.01 <i>M</i> K_2SO_4	180	56	315	600	
Saturated lead sulfate ^a	45	16	67	300	
Saturated lead sulfate ^a	180	6	11	43	
Standard lead, 0.1 <i>M</i> in HNO_3	45	48	180	450	

^a Reverse precipitation.

The speed of penetration of thorium B decreases very rapidly upon aging of the precipitate in the standard lead solution, as is demonstrated clearly by the curves in Fig. 1. Values greater

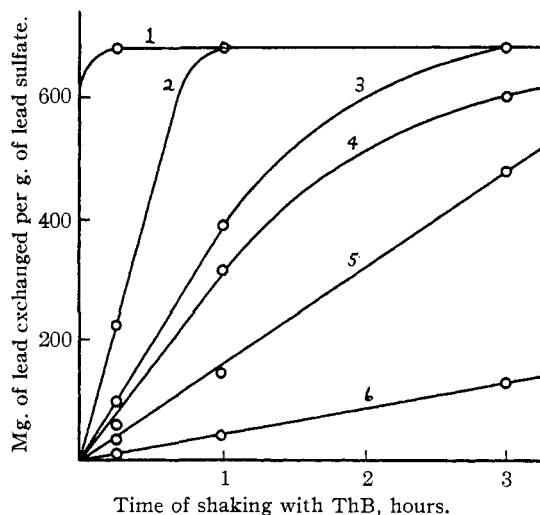


Fig. 1.—Lead sulfate aged in standard lead solution at 25°: 1, fresh; 2, aged 12 min.; 3, 20 min.; 4, 45 min.; 5, 57 min.; 6, 3 hours.

than 680 mg. of lead exchanged per 1 g. (100% of exchange) have been reduced to this value. As pointed out in previous papers,² a small error in the radioactive measurements causes a large deviation from 680. It should be mentioned that an apparent exchange of more than 100% may be found, however, as a result of heterogeneous distribution of the thorium B.

The precipitates behave much like lead sulfate obtained from 0.1 *M* solutions.^{2a} The speed of aging is most pronounced as an equivalent body, and it decreases with increasing lead or sulfate concentration in the aging medium. The rate of aging is of the same order in an excess of lead as in the same excess of sulfate. These results are in agreement with a previous conclusion, that the speed of perfection (aging), and consequently the speed of recrystallization, decrease with decreasing solubility of the lead sulfate in the aging medium. When the solubility is increased, *e. g.*, by the addition of nitric acid, the speed of aging becomes more pronounced as indicated by some experiments in Table III.

Specific Surface.—In the following the rate of aging as indicated by the wool violet adsorption was studied. In the first place it was shown that the amounts of wool violet adsorbed were the same, immaterial whether the dye was added before or after filtration of the lead sulfate, when the latter was kept wet. When the precipitate was made air-dry the amount of dye adsorbed was found to be 20 to 25% less, probably as a result of clustering of some of the particles. If, before adding the dye, such an air-dried product was shaken vigorously for five minutes or longer with a saturated lead sulfate solution in water, the clusters were broken up and the same amount of dye was found adsorbed as before filtration. In the following experiments the products were not made air-dry after filtration. The amounts of wool violet adsorbed after aging under various conditions are given in Table IV.

The most pronounced decrease of the surface occurs during the early stages of aging; in this period the speed of perfection of the precipitate is also the greatest (see Table III). When the speed of perfection is decreased, *e. g.*, by adding an excess of lead nitrate or potassium sulfate (Table III) the speed of decrease of the specific surface is also decreased (Table IV). Again, the same

TABLE IV
AMOUNT OF WOOL VIOLET ADSORBED ON THE SATURATED SURFACE OF LEAD SULFATE OBTAINED FROM 0.0665 *M* SOLUTIONS (DIRECT PPT.) AFTER AGING UNDER VARYING CONDITIONS

Aging medium	Wool violet adsorbed in mg. per gram after aging for				
	0	0.2	1	3	24 hours
Standard lead	2.6	1.8	1.6	1.2	1.1
Standard sulfate			1.6	1.2	1.2
0.01 <i>M</i> Pb(NO ₃) ₂		2.1	1.7	1.4	
.1 <i>M</i> Pb(NO ₃) ₂		2.3		1.9	1.5
.01 <i>M</i> K ₂ SO ₄		2.3	1.7	1.5	1.2

speed of aging, as indicated by the decrease of the specific surface, was found in an excess of lead as in excess of sulfate.

Summary

1. Filtration or centrifuging has no effect upon the aging of lead sulfate prepared under conditions given in this paper.
2. The huge apparent effect of filtration or centrifuging was found to be due to a slight coprecipitation of some basic salt with the lead sulfate. The effect can be eliminated by adding acid to the solution containing thorium B solution.
3. Evidence has been presented that the coprecipitated basic salt is located on active surface.
4. The speed of perfection and the speed of decrease of the specific surface upon aging decrease with increasing lead or sulfate concentration in the aging medium, excess of lead having quantitatively about the same effect as the same excess of sulfate.
5. Precipitates obtained by reverse precipitation have a larger specific surface and age more rapidly than products obtained by direct precipitation. During precipitation of the former there is a possibility of the formation of the double salt PbSO₄·K₂SO₄ which, after precipitation, is rapidly transformed into PbSO₄.

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