Summary

The use of ozone as an initiator of reaction between ethylene and oxygen at temperatures below the normal reaction temperature in absence of ozone has been studied.

The results are consistent with the hypothesis that the oxidation process is a chain reaction.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

SOLUBILITY OF LEAD SULFATE, CHROMATE AND MOLYBDATE IN NITRIC AND IN PERCHLORIC ACID

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It has been shown by Thiel and Stoll[2] that the difference in potential between lead electrodes in 0.05 molar solutions of lead perchlorate and nitrate is 0.016 volt. From this they calculated the ratio of the concentrations of Pb^{++} in the two solutions to be 1:0.28. In connection with other work the present authors had noticed that lead sulfate, chromate and molybdate were less soluble in perchloric acid than in nitric acid of the same concentration. In order to investigate this matter more thoroughly, with the possibility of utilizing the results in analytical separations, the solubilities of these salts were determined in perchloric and in nitric acids of different concentrations, both with and without the addition of a common ion.

Experimental

Preparation of Lead Sulfate.—Lead sulfate was prepared by adding simultaneously from two burets dilute solutions of sulfuric acid and lead perchlorate to 800 cc. of slightly acidified water, with vigorous stirring. This gave a fairly coarse precipitate. It was washed with water five times by decantation, centrifuged in platinum cups and washed four times on the centrifuge.

Preparation of Lead Chromate.—Lead chromate was prepared in the same manner as lead sulfate, using lead perchlorate and potassium dichromate. The lead chromate was washed with water eight times by decantation, four times on the centrifuge, dried in a vacuum over phosphorus pentoxide and analyzed by electrometric titration with ferrous sulfate. The average of two closely agreeing analyses gave 16.09% chromium, compared to a theoretical value of 16.08%.

Preparation of Lead Molybdate.—Lead molybdate was prepared in a similar manner by adding lead perchlorate and ammonium molybdate to hot water acidified with perchloric acid. After boiling the solution for a few minutes, the precipitate was washed eight times by decantation with hot 2% ammonium nitrate solution, centrifuged, and

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[1] From a dissertation submitted by J. L. Kassner to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Thiel and Stoll, Z. anorg. allgem. Chem., 139, 317 (1924).

washed eight times on the centrifuge. Since it has been pointed out by Weiser[3] that lead molybdate occludes ammonium molybdate, the salt was further purified by stirring about 10 g. in a liter of normal perchloric acid for twenty-four hours. After it had settled, a 500-cc. sample of the clear solution was analyzed for lead and molybdenum and found to contain an excess of the latter, which must have been occluded as ammonium molybdate and subsequently extracted by the acid. The lead molybdate which had been stirred in perchloric acid was centrifuged and washed with hot 2% ammonium nitrate. After ignition it was analyzed, lead and molybdenum being separated by the sulfide method.[4]

Anal. Calcd.: PbO, 60.78. Found: 60.72, 60.76, 60.69, average, 60.72. Calcd.: MoO_3, 39.22. Found: 39.18, 39.14, 39.11, average, 39.14.

The lead molybdate possessed a yellowish-white tinge. This was also observed by Weiser.[3]

Preparation of Nitric and Perchloric Acids.—c. p. perchloric and nitric acids were redistilled in a vacuum. The different concentrations were made up from these by means of a hydrometer, using for perchloric acid the table by van Emster[5] and for nitric acid the densities given by Lunge and Ray.[6] The hydrometers were calibrated to read directly to 0.0005 at 15.5° and it was possible to estimate to 0.0001. The accuracy of this method of making up the acid concentrations was checked by titrating with standard alkali. The maximum error was about 0.002 M for higher concentrations and much less than this for the very dilute solutions.

Solubility Determinations.—Lead sulfate, lead chromate and lead molybdate were each placed in liter flasks and rotated with known concentrations of nitric and perchloric acids, respectively, in a thermostat which was not observed to vary as much as 0.001°. The water used in the acid solutions was twice distilled, using a block tin condenser and a quartz receiver. The flasks were closed with well ground stoppers covered with sheet rubber to keep the water in the thermostat from contact with the ground-glass joint. They were rotated for fifteen hours, then supported in a vertical position for two hours and the salt allowed to settle. Although the supernatant liquid was clear, the solutions were filtered through a platinum sponge filtering crucible into which they were siphoned directly from the flasks, the first portion being discarded. In this way it was possible to obtain samples absolutely free from particles of salt. A 500-cc. sample was taken for the low solubilities, and a 250- or 100-cc. sample for some of the higher ones. The results shown are the average of closely agreeing duplicates.

Solubility of Lead Sulfate in Perchloric and Nitric Acids.—Saturation of the solutions was carried out in quartz flasks with ground stoppers. After rotating lead sulfate in the thermostat as described, a 500-cc. sample was measured out, 1 cc. of concentrated sulfuric acid added and the solution

[3] Weiser, *J. Phys. Chem.*, **20**, 640 (1916).

[4] Treadwell–Hall, "Quantitative Analysis," 7th ed., Vol. II, John Wiley and Sons, Inc., New York, **1928**, p. 266.

[5] Van Emster, *Z. anorg. Chem.*, **52**, 270 (1907).

[6] Lunge and Ray, *Z. angew. Chem.*, **4**, 165 (1891).

concentrated in a quartz evaporating dish to about 25 cc. It was then transferred to a tared crucible, evaporated to dryness by means of a ring burner, and ignited at low red heat. It was possible to reproduce the weight of the crucible to within 0.05 mg. when the tare was ignited and cooled in the same way as the sample before each weighing. If the tare was not ignited each time, the variation was 0.1 mg. or more.

Solubility of Lead Sulfate Using a Common Ion.—The procedure was essentially the same except that the solutions were made up carefully from standard solutions so that when they were mixed and diluted to the required amount, the normalities would be as indicated in the tables. All the samples in which sulfuric acid furnished the common ion were analyzed by direct evaporation as explained above, except in a few cases in which the solubility was so low that lead was determined colorimetrically as sulfide.[7]

As there were no interfering substances present, the procedure was much simplified. A 500-cc. sample of the clear supernatant liquid was evaporated on the hot-plate and fumed until all the sulfuric acid was removed. The residue of lead sulfate was dissolved in ammonium acetate solution and diluted until the concentration of lead ion was low enough to determine colorimetrically, as determined by a preliminary test. Of this diluted solution, 25, 50 or 100 cc. (depending on the amount of lead present) was made ammoniacal with 5 cc. excess of concentrated ammonia water and diluted to a definite volume, as 100 cc. Lead sulfide was precipitated by adding 4 or 5 drops of the sodium sulfide solution. A standard was prepared in the same way and its color compared with that of the unknown. A blank was run in each case on the unknown before adding sodium sulfide. It was possible to check results within 5%.

In the solubilities in which lead perchlorate and lead nitrate furnished the common ion, it was necessary to determine the sulfate ion. This was done by removing most of the lead electrolytically from the original solution, concentrating the sample to about 75 cc. and removing the remaining lead. The solution was partially neutralized with sodium carbonate, after which the sulfate was precipitated with barium chloride. The weight of lead sulfate was calculated from the weight of barium sulfate obtained. The results are shown in Tables I and II.

It is interesting to note that the solubility of lead sulfate in perchloric acid increases up to a 2.0 M solution of acid and then decreases again, while the solubility of lead sulfate in nitric acid continues to increase with increasing acid concentration. Lead sulfate is much less soluble in perchloric acid than in nitric acid of the same concentration.

Solubility of Lead Chromate.—Saturation of the solutions with lead chromate was carried out in glass flasks with ground stoppers. The

[7] Scott, "Standard Methods of Chemical Analysis," 4th ed., D. Van Nostrand Co., New York, 1925, p. 281.

<div align="center">TABLE I</div>

<div align="center">SOLUBILITY OF LEAD SULFATE IN PERCHLORIC ACID AT 25°</div>

	PbSO₄ dissolved in 100 cc.	
Composition of solvent	G.	Millimole
0.1 M HClO₄	0.0278	0.0917
0.1 M HClO₄ + 0.005 M H₂SO₄	.0070	.0230
0.1 M HClO₄ + 0.02 M H₂SO₄	.0024	.0079
0.1 M HClO₄ + 0.05 M H₂SO₄	.0013	.0043
0.1 M HClO₄ + 0.10 M H₂SO₄	.0010^a	.0033
0.1 M HClO₄ + 0.25 M H₂SO₄	.0008^a	.0026
0.1 M HClO₄ + 0.50 M H₂SO₄	.0003^a	.0010
0.1 M HClO₄ + 0.50 M Pb(ClO₄)₂	.0002	.0007
0.5 M HClO₄	.0528	.1742
0.5 M HClO₄ + 0.005 M H₂SO₄	.0206	.0679
0.5 M HClO₄ + 0.01 M H₂SO₄	.0137	.0451
0.5 M HClO₄ + 0.02 M H₂SO₄	.0067	.0220
0.5 M HClO₄ + 0.05 M H₂SO₄	.0030	.0099
1.0 M HClO₄	.0714	.2301
1.0 M HClO₄ + 0.005 M H₂SO₄	.0367	.1211
2.0 M HClO₄	.0787	.2596
3.0 M HClO₄	.0687	.2266
4.2 M HClO₄	.0490	.1616

^{a} Lead determined colorimetrically.

<div align="center">TABLE II</div>

<div align="center">SOLUBILITY OF LEAD SULFATE IN NITRIC ACID AT 25°</div>

	PbSO₄ dissolved in 100 cc.	
Composition of solvent	G.	Millimole
0.1 M HNO₃	0.0426	0.1405
0.1 M HNO₃ + 0.005 M H₂SO₄	.0078	.0257
0.1 M HNO₃ + 0.05 M H₂SO₄	.0015	.0049
0.1 M HNO₃ + 0.25 M H₂SO₄	.0011	.0036
0.1 M HNO₃ + 0.50 M H₂SO₄	.0009	.0030
0.1 M HNO₃ + 0.50 M Pb(NO₃)₂	.0008	.0026
0.5 M HNO₃	.0992	.3272
0.5 M HNO₃ + 0.005 M H₂SO₄	.0398	.1313
0.5 M HNO₃ + 0.01 M H₂SO₄	.0328	.1082
0.5 M HNO₃ + 0.02 M H₂SO₄	.0159	.0524
0.5 M HNO₃ + 0.05 M H₂SO₄	.0089	.0293
1.0 M HNO₃	.2021	.6667
1.0 M HNO₃ + 0.005 M H₂SO₄	.1007	.3322
2.0 M HNO₃	.3605	1.1890
3.0 M HNO₃	.5389	1.7770
4.2 M HNO₃	.7263	2.3960

amount of lead chromate dissolved in the various concentrations of perchloric acid was determined by adding potassium iodide and titrating the iodine liberated with sodium thiosulfate using starch as indicator. For those in nitric acid the lead chromate was titrated electrometrically with 0.1 or 0.01 N ferrous sulfate. The solutions were concentrated to 150–200 cc., with addition of sulfuric acid when necessary, and cooled in ice

before titrating. When lead perchlorate and lead nitrate furnished the common ion, the chromate was determined by electrometric titration with ferrous sulfate. When sodium dichromate was used, the solution was analyzed for lead by reducing the dichromate with hydroxylamine hydrochloride, adjusting the acidity of the solution, and precipitating the lead with hydrogen sulfide. The lead sulfide was filtered, washed and dissolved in dilute nitric acid. This solution was boiled, neutralized and diluted to a suitable definite volume. Lead was then determined colorimetrically as described above. The results are shown in Tables III and IV.

TABLE III

SOLUBILITY OF LEAD CHROMATE IN PERCHLORIC ACID AT 25°

Composition of solvent	PbCrO₄ dissolved in 100 cc. G.	Millimole
0.1 M HClO₄	0.0041	0.0127
0.1 M HClO₄ + 0.005 M Pb(ClO₄)₂	.0000	.0000
0.5 M HClO₄	.0120	.0371
0.5 M HClO₄ + 0.005 M Pb(ClO₄)₂	.0005	.0015
0.5 M HClO₄ + 0.01 M Pb(ClO₄)₂	.0000	.0000
1.0 M HClO₄	.0140	.0433
1.0 M HClO₄ + 0.005 M Pb(ClO₄)₂	.0013	.0040
1.0 M HClO₄ + 0.01 M Pb(ClO₄)₂	.0000	.0000
2.0 M HClO₄	.0199	.0616
2.0 M HClO₄ + 0.01 M Pb(ClO₄)₂	.0012	.0037
2.0 M HClO₄ + 0.015 M Pb(ClO₄)₂	.0006	.0019
3.0 M HClO₄	.0211	.0668
4.0 M HClO₄	.0213	.0659
5.0 M HClO₄	.0191	.0591
5.0 M HClO₄ + 0.02 M Pb(ClO₄)₂	.0001	.0003
5.0 M HClO₄ + 0.03 M Na₂Cr₂O₇	.0000	.0000

TABLE IV

SOLUBILITY OF LEAD CHROMATE IN NITRIC ACID AT 25°

Composition of solvent	PbCrO₄ dissolved in 100 cc. G.	Millimole
0.1 M HNO₃	0.0063	0.0195
0.1 M HNO₃ + 0.005 M Pb(NO₃)₂	.0001	.0003
0.1 M HNO₃ + 0.01 M Pb(NO₃)₂	.0000	.0000
0.5 M HNO₃	.0177	.0548
0.5 M HNO₃ + 0.005 M Pb(NO₃)₂	.0018	.0055
0.5 M HNO₃ + 0.01 M Pb(NO₃)₂	.0000	.0000
1.0 M HNO₃	.0385	.1190
1.0 M HNO₃ + 0.01 M Pb(NO₃)₂	.0038	.0117
2.0 M HNO₃	.0889	.2752
2.0 M HNO₃ + 0.15 M Pb(NO₃)₂	.0012	.0037
2.0 M HNO₃ + 0.25 M Pb(NO₃)₂	.0002	.0006
2.0 M HNO₃ + 0.30 M Na₂Cr₂O₇	.0002	.0006
3.0 M HNO₃	.1701	.5265
3.0 M HNO₃ + 0.02 M Pb(NO₃)₂	.0381	.1179
4.0 M HNO₃	.2812	.8700
5.0 M HNO₂	.4367	1.3510

In the case of lead chromate the solubility in perchloric acid increases up to 4.0 M acid and then begins to decrease, while the solubility in nitric acid continues to increase with increasing concentration of acid. Lead chromate is much less soluble in perchloric acid than in nitric acid of the same concentration.

Solubility of Lead Molybdate.—The solubility determinations of lead molybdate were carried out like those for lead chromate, and the supernatant liquid analyzed for both lead and molybdenum. This was done by adding 4–6 cc. of concentrated sulfuric acid and evaporating to remove the perchloric acid or nitric acid. The solution was diluted, the lead sulfate filtered off, washed with 0.5% sulfuric acid, ignited and weighed. If molybdenum is carried down it is detected by a bluish tinge around the edge of the precipitate during ignition. After adjusting the acidity of the filtrate, the molybdenum was reduced to a trivalent salt by passing it through a Jones reductor, received in a ferric alum and phosphoric acid solution and titrated with permanganate.[8] Perchloric acid must be absent because it oxidizes trivalent molybdenum even in dilute solution. The solubilities were discontinued at 1 M nitric and 3 M perchloric acid, because the molybdate seemed to be decomposed by the more concentrated acids, forming MoO_3.

Two methods were used for determining the solubilities of lead molybdate when lead perchlorate and lead nitrate furnished the common ion. First, when the concentration of the salt giving the common ion was not greater than 0.05 M, the procedure was the same as that above, except that the supernatant liquid was analyzed only for molybdenum. With lower solubilities, where greater accuracy was required, the colorimetric method of King[9] was used, with certain modifications. A 500-cc. sample was prepared by evaporating to fumes with a slight excess of sulfuric acid. The lead sulfate was filtered off and the molybdenum determined colorimetrically. Fifty cc. of the solution containing 2–3 cc. of concd. hydrochloric acid, about 2 cc. of concd. sulfuric acid and 1.5 g. of potassium thiocyanate was placed in a separatory funnel with the ether and cooled to 0°; 1 cc. of stannous chloride solution was added and the mixture shaken immediately. Two ether extractions were made, using 70 and 30 cc., respectively, but no color was obtained in the second.

When sodium molybdate furnished the common ion, the lead was separated by a double precipitation with alkaline sulfide,[4] converted into sulfate, dissolved in ammonium acetate to free it from silica, and determined colorimetrically.[7]

The results are shown in Tables V and VI.

Lead molybdate, like the sulfate and chromate, is much less soluble in

[8] Ref. 7, p. 319.
[9] King, *Ind. Eng. Chem.*, **15**, 350 (1923).

TABLE V

SOLUBILITY OF LEAD MOLYBDATE IN PERCHLORIC ACID AT 25°

Composition of solvent	PbMoO₄ in 100 cc.	
	G.	Millimole
0.10 M HClO₄	0.0016	0.0043
0.10 M HClO₄ + 0.01 M Pb(ClO₄)₂	.0002	.0005
0.50 M HClO₄	.0136	.0370
0.50 M HClO₄ + 0.01 M Pb(ClO₄)₂	.0005	.0013
0.50 M HClO₄ + 0.02 M Pb(ClO₄)₂	.0004	.0011
0.50 M HClO₄ + 0.10 M Pb(ClO₄)₂	.00006[a]	.0001
0.50 M HClO₄ + 0.20 M Pb(ClO₄)₂	.00004[a]	.0001
0.50 M HClO₄ + 0.02 M Na₂MoO₄	.0004[b]	.0011
0.50 M HClO₄ + 0.05 M Na₂MoO₄	.00027[b]	.0007
1.0 M HClO₄	.0373	.1016
2.0 M HClO₄	.1176	.3204
3.0 M HClO₄	.2436	.6639

[a] Mo determined colorimetrically.   [b] Pb determined colorimetrically.

TABLE VI

SOLUBILITY OF LEAD MOLYBDATE IN NITRIC ACID AT 25°

Composition of solvent	PbMoO₄ dissolved in 100 cc.	
	G.	Millimole
0.10 M HNO₃	0.0020	0.0060
0.50 M HNO₃	.0244	.0665
0.50 M HNO₃ + 0.10 M Pb(NO₃)₂	.00032[a]	.0009
0.50 M HNO₃ + 0.20 M Pb(NO₃)₂	.0002[a]	.0005
0.50 M HNO₃ + 0.02 M Na₂MoO₄	.00064[b]	.0017
0.50 M HNO₃ + 0.50 M Na₂MoO₄	.0007[b]	.0019
1.0 M HNO₃	.1086	.2958

[a] Mo determined colorimetrically.   [b] Pb determined colorimetrically.

perchloric acid than in nitric acid of the same concentration. The solubilities could not be carried far enough to determine whether it would pass through a maximum in perchloric acid as with lead sulfate and chromate.

The solubilities suggest a number of quantitative separations which are now being investigated.

Summary

1. The solubilities of lead sulfate, chromate and molybdate have been determined in perchloric and nitric acids, both with and without the addition of a common ion.

2. All these salts are much less soluble in perchloric acid than in nitric acid of the same concentration.

3. Both the sulfate and chromate pass through a maximum solubility in perchloric acid, and then, as the concentration of acid increases, the solubility decreases.

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