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Acetometallates. I. Acetoplumbites

BY ALEXANDER LEHRMAN AND EDGAR LEIFER

It has been shown that the solubility of metal hydroxides in strong solutions of alkali metal hydroxides is due to the formation of metal hydroxyl complex ions.[1] In the case of plumbous hydroxide Brintzinger and Wallach[2] showed from rate of diffusion experiments that probably many different hydroxyl plumbites exist, while Scholder and Patsch[3] showed the probable existence of tri-, tetra- and hexahydroxylplumbites. The salts potassium tri-, tetra- and hexahydroxylplumbite can be considered to be addition compounds of potassium hydroxide and plumbous hydroxide. However, they cannot be prepared directly from these substances in a binary system as plumbous hydroxide decomposes on heating.

Davidson and co-workers[4] showed the analogy between acetometallates and hydroxylmetallates. In some cases they obtained acetometallates which corresponded exactly in formula to known hydroxylmetallates. It was therefore thought that an investigation of the liquidus curve of the binary system potassium acetate–plumbous acetate would be of value in that it would show which acetoplumbites exist. There should be some analogy between these and the hydroxylplumbites. Furthermore, as was pointed out by Sandved[5] there is much evidence that stable complex lead acetates exist, though outside of the compound $2Pb(C_2H_3O_2)_2\cdot HC_2H_3O_2$ prepared by Tarbutton and Vosburgh[6] and which may be considered to be an acid whose anion is a complex acetoplumbite, none have been isolated.

Experimental

Materials.—Potassium acetate of C. P. grade was recrystallized from distilled water, dried in an oven above 100° for one week and then bottled. Before weighing out portions it was dried again for six hours at 140°. Its melting point was 292°, which agrees with the value given in the "I. C. T."[7]

Lead acetate of C. P. grade was recrystallized from distilled water acidified with acetic acid (1 ml. of glacial acetic acid to 100 ml. of solution). It was then dried at 100°. Its melting point, 204°, corresponds to that given by Petersen.[8] It is well to note here that the "I. C. T." value,[9] 280°, is incorrect. Beilstein[10] gives this same value which is taken from Gmelin.

Temperature Measurements.—Some of the temperatures were measured with a copper–constantan thermocouple of No. 24 wire in conjunction with a Leeds and Northrup potentiometer indicator, the cold junction being cracked ice. The couple was protected from the molten compounds by a narrow guard tube made by drawing out Pyrex tubing and sealing at one end. It was standardized by determining the e. m. fs. at the boiling point of water, the eutectic point of tin and lead (183°), and the melting points of U. S. Bureau of Standards tin (231.9°) and purified potassium nitrate (333°), and plotting the deviations from the standard table of Adams.[11] For some of the points a mercury thermometer was used. This thermometer was calibrated, in the apparatus used, against the thermocouple used for the other points.

Method.—Mixtures of potassium acetate and lead acetate (total weight between 20 and 35 g.) were weighed into 2.5 × 20 cm. Pyrex tubes. The weights were taken to the nearest centigram. The lead acetate, having the lower melting point, was always the top one of the two salts. The couple in its guard tube or the thermometer was inserted and the tube then suspended in a bath of the molten eutectic mixture of the nitrates of lithium, potassium and calcium.[12] The bath was heated slowly until the lead acetate melted and ran into the potassium acetate. At a somewhat higher temperature the mixture quickly became entirely liquid. On cooling with vigorous stirring, crystallization took place. The bath was then heated slowly, the molten acetates stirred with the thermocouple guard tube and the temperature at which the last crystal disappeared was noted.

Some of the mixtures rich in potassium acetate start to decompose at the high temperatures needed to melt them. The addition of two drops of glacial acetic acid was found to prevent this. While most of the added acetic acid volatilized, some probably remained and affected the observed temperature of complete melting. However, the error is probably slight and in no way will affect the shape of the curve obtained. In some cases there was a considerable tendency to supercool and inoculation with a tiny particle of a previously crystallized melt was then resorted to. Due to this tendency to supercool, time–temperature cool-

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(1) Scholder, *Z. angew. Chem.*, **46**, 509 (1933).

(2) Brintzinger and Wallach, *ibid.*, **47**, 61 (1934).

(3) Scholder and Patsch, *Z. anorg. allgem. Chem.*, **217**, 214 (1934); *ibid.*, **220**, 209 (1934).

(4) Davidson and McAllister, THIS JOURNAL, **52**, 519 (1930); Davidson, *Chem. Rev.*, **8**, 175 (1931); Davidson and Griswold, THIS JOURNAL, **53**, 1341 (1931); *ibid.*, **57**, 425 (1935).

(5) Sandved, *J. Chem. Soc.*, 2967 (1927).

(6) Tarbutton and Vosburgh, THIS JOURNAL, **54**, 4537 (1932).

(7) "International Critical Tables," Vol. I, p. 155.

(8) Petersen, *Z. Elektrochem.*, **20**, 328 (1914).

(9) "International Critical Tables," Vol. I, p. 117.

(10) Beilstein, "Handbuch der organische Chemie," Band II, System 158, Verlag von Julius Springer, Berlin, 1920.

(11) "Pyrometric Practice," U. S. Bureau of Standards Technological Paper No. 170, p. 309.

(12) Lehrman, *et al.*, THIS JOURNAL, **59**, 179 (1937).

ing curves could not be used to obtain initial crystallization temperatures, but were used to obtain three of the eutectic temperatures. The temperature measurements were repeated until they agreed to within 1°. Each value reported represents at least two determinations.

Results and Discussion

Temperatures of disappearance of the last crystal and eutectic points are given in the following table and plotted in Fig. 1.

THE SYSTEM POTASSIUM ACETATE-LEAD ACETATE

$Pb(C_2H_3O_2)_2$, mole %	Melting temp., °C.	Eutectic halt, °C.
0	292	
13.6	278	
20.1	259	
25.9	227	
28.3	221	174.9
30.6	181	
33.7	183	
39.7	182	
44.3	180	
44.6	180	
47.4	190	169.5
50.6	194	
50.8	193	
55.2	180	
58.0	177	
60.6	162	
62.5	159	
65.3	169 (148) metastable	
66.8	169	
71.2	164	
78.1	134	132.2
83.1	168	
90.8	188	
100.0	204	

The data show the existence of the compounds $KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$, $2KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$ and $KC_2H_3O_2 \cdot 2Pb(C_2H_3O_2)_2$. These indicate the probable existence of triaceto- and tetraacetoplumbite ions as well as pentaacetodiplumbite ion $(Pb_2(C_2H_3O_2)_5)^-$. The compounds $KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$ and $2KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$ are formally analogous to the compounds $NaPb(OH)_3$ and $Na_2Pb(OH)_4$ obtained by Scholder and Patsch.[3] The compound $KC_2H_3O_2 \cdot 2Pb(C_2H_3O_2)_2$ is related to the compound $2Pb(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ and suggests that this solvate is an acid of the formula $H[Pb_2(C_2H_3O_2)_5]$.

By analogy to the compound $Na_4Pb(OH)_6$ obtained by Scholder, the system potassium acetate-lead acetate should show a region with a maximum at 20 mole per cent. of lead acetate. Cooling curves could not be run in this region due to the high viscosity and resulting supercooling. The curve is very steep at 20 mole per cent. of lead acetate and the errors involved in this region prevent a detection of the supposed compound from the curve alone.

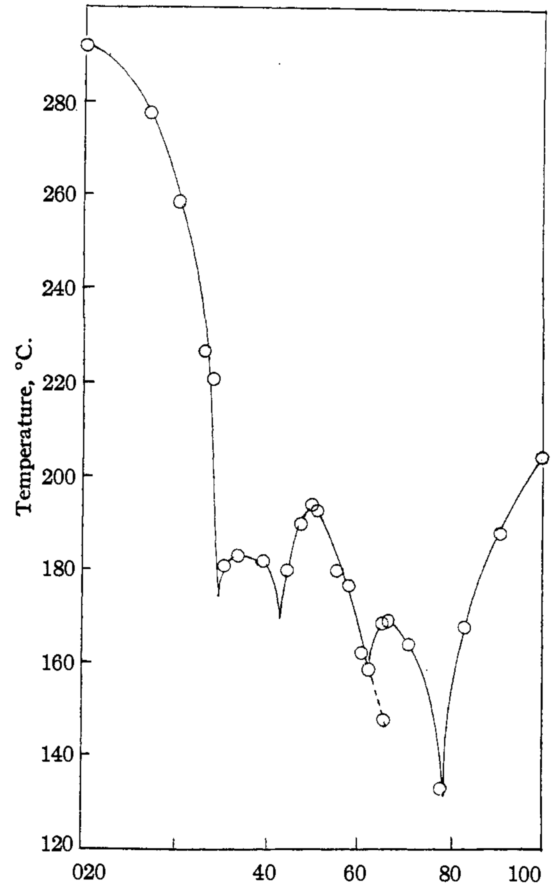

Fig. 1.—Mole per cent. of lead acetate.

Just before the work described here was completed, a paper by Griswold and Olson appeared[13] describing some work on the system sodium acetate-lead acetate-acetic acid. The authors obtained the previously known $2Pb(C_2H_3O_2)_2 \cdot HC_2H_3O_2$ and $NaC_2H_3O_2 \cdot 2HC_2H_3O_2$ but no addition compound of sodium acetate and lead acetate nor a compound of the three components. Their failure to obtain the addition compounds can be ascribed either to the high viscosity of their solutions or to the possibilities that these addition compounds do not exist at 30° or at 30° do not exist in equilibrium with acetic acid.

Summary

1. The liquidus curve of the binary system potassium acetate-lead acetate has been determined.
2. The following compounds have been shown

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[13] Griswold and Olson, THIS JOURNAL, 59, 1894 (1937).

to exist: $KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$, $2KC_2H_3O_2 \cdot Pb(C_2H_3O_2)_2$ and $KC_2H_3O_2 \cdot 2Pb(C_2H_3O_2)_2$.

3. The analogy between these compounds and the hydroxyl plumbites has been shown.

4. It is suggested that the solvate $Pb(C_2H_3O_2)_2 \cdot 0.5HC_2H_3O_2$ is a complex acetoplumbous acid.

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Catalysis of Nitramide Decomposition by Colloidal Platinum and Gold

BY CECIL V. KING

In a previous study, it was found that the decomposition of nitramide in aqueous solution

$$H_2N_2O_2 \longrightarrow H_2O + N_2O$$

was accelerated by platinized electrodes.[1] This suggested an investigation of the catalysis by colloidal and finely divided metals, and experiments with platinum and gold are reported in this paper.

At 20° the "spontaneous" (water-catalyzed) pseudo-unimolecular decomposition of nitramide has a half-time of about six hours. In dilute solutions of strong acids the rate is practically independent of the acid concentration, although a very small acid catalysis has been reported.[2] The colloidal metal catalysis can then be studied in dilute acid solutions, but not in alkaline media because of the large catalytic effect of bases.

In many respects the catalysis reported here resembles the colloidal metal catalysis of hydrogen peroxide decomposition, studied extensively by Bredig and his collaborators and by many investigators since. Brief reviews of this work are found in a number of publications.[3] The catalysis is now ascribed to a rapid decomposition of hydrogen peroxide adsorbed on the surface of the colloidal particles.[4] The inhibiting effect of many substances is ascribed to their preferential adsorption and partial or complete displacement of the hydrogen peroxide. The mechanism of the decomposition in the adsorbed phase has been studied and discussed by Weiss.[5]

Materials and Method

Nitramide was prepared by the customary method,[6] the final extraction being made as described by Marlies and La Mer.[7] It was recrystallized by dissolving in ether, adding chloroform and partly evaporating the solution *in vacuo*.

Six preparations of colloidal platinum were used. These were made by striking a direct current arc between platinum wires immersed in well-stirred distilled water, cooled in an ice-bath. In preparing sols I–V, inclusive, the current was kept at approximately four amperes; in making sol VI, three amperes. Two gold sols were made with a current of three amperes; sol I in 0.0001 *M* hydrochloric acid, sol II in 0.0002 *M* acid. Gold sol IIA consisted of residues from experiments in which sol II was diluted with water only (15 cc. sol II to 50 cc.), nothing else being added except nitramide samples.

Metal Content of the Sols.—No attempt was made to analyze the sols with great accuracy. The metal content was determined as indicated in Table I, 50-cc. samples being used in most cases. The evaporation residue was dissolved in aqua regia and finally converted to the chloro salt by adding a weighed amount (in excess) of potassium chloride. The gold sols showed no discrepancy between the weight of the residue from evaporation and the gold content of the chloroaurate. The metal content of the platinum sols, however, varies from 10 to 30% less than the weight of the residue from evaporation, indicating that this residue contains other material than the metal. It has been known that some of the platinum is oxidized in preparing such sols; Pennycuick[8] has estimated that about

TABLE I

COMPOSITION OF THE SOLS

Sol. no.	Residue on evaporation g./l.	Metal from chloro salt
	Platinum	
I	0.050[a]	...
II	.106	0.092
III	.068	.058
IV	.038	.022
V	.114	.104
VI	.070	.053
	Gold	
I	.204	.205
II	.204	.205
IIA	.0612[b]	...

[a] Determined by precipitating with hydrochloric acid.
[b] Calculated from dilution of sol II.

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[1] Brönsted and King, THIS JOURNAL, **49**, 193 (1927).

[2] Marlies and La Mer, *ibid.*, **57**, 1812 (1935).

[3] Freundlich, "Colloid and Capillary Chemistry," English translation of 3d German edition, Methuen and Co., London, 1926. Weiser, "Inorganic Colloid Chemistry," John Wiley and Sons, Inc., New York, 1933. A volume of the series "Kolloidforschung in Einzeldarstellungen" to deal exclusively with this subject has not appeared.

[4] MacInnes, THIS JOURNAL, **36**, 878 (1914).

[5] Weiss, *Trans. Faraday Soc.*, **31**, 1547 (1935).

[6] Thiele and Lachman, *Ann.*, **292**, 317 (1896).

[7] Marlies and La Mer, THIS JOURNAL, **57**, 2008 (1935).

[8] Pennycuick, *ibid.*, **52**, 4621 (1930), and previous papers.