

brownish-white crystals. These were drained and recrystallized from benzene several times, when the compound was obtained in white granular crystals melting at 117–118°. The yield was very small.

Analyses. Subs., 0.0942: CO₂, 0.1435; H₂O, 0.0511. Subs., 0.0753: 9.7 cc. N₂ (30° and 761 mm.). Calc. for C₁₀H₁₆O₅N₃Cl: C, 40.89; H, 5.45; N, 14.31. Found: C, 41.54; H, 6.03; N, 14.32.

IMIDE CHLORIDE, CH₂ClCH(NCOOC₂H₅)₂NCl.—The substance was dissolved in boiling water and filtered through a hot filter into a beaker placed on a bath of warm water, and a current of chlorine was passed through the solution at the same time. As the addition of the chlorine was continued the crystals deposited at the bottom of the vessel began to turn soft and pasty and the solution became turbid. At this stage the current of chlorine was shut off and the solid filtered by suction and dried on a porous plate. On recrystallization in the cold, it is obtained in the shape of granular crystals melting at 75–76°. The substance is unstable and decomposes gradually with the evolution of chlorine.

Analyses. Subs., 0.1056: 35.8 cc. 0.1 *N* thiosulfate solution. Calc. for C₅H₁₃O₄N₃-Cl₂: Cl as =N.Cl, 12.41. Found: 12.06.

Dichlorocarbamic Methyl Ester, NCl₂.COOCH₃.—Two g. of methyl carbamate was dissolved in 20 cc. of water and a current of chlorine was passed through it when a yellow oil separated at the bottom. The separation of the oil was very slow at first but after a time it was very rapid. The current of chlorine was stopped when no more oil formed. The oil was separated, washed with water and dried over calcium chloride. The yield was nearly quantitative.

Analysis. Subs., 0.1863: 26.3 cc. of 0.1 *N* thiosulfate solution. Calc. for C₂H₅O₂-NCl₂: Cl, as =NCl, 49.31. Found: 50.12.

Investigations on similar lines are being continued.

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CALCUTTA, INDIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

THE OXIDATION OF POTASSIUM ACETATE TO POTASSIUM OXALATE¹

BY WILLIAM LLOYD EVANS AND PAUL R. HINES

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The following experiments on the oxidation of potassium acetate to potassium oxalate were carried out because the literature contains conflicting data in reference to the possibility of such a reaction. Under chosen experimental conditions oxalic acid is obtained as an oxidation product when certain methyl-containing compounds such as ethyl alcohol and acetaldehyde are oxidized with alkaline potassium permanganate. It became of much interest, therefore, to know whether acetates were oxidized to oxalates with neutral or with alkaline solutions of permanga-

¹ Presented at the New York meeting of the American Chemical Society, September, 1921.

nates; and, if so, under what conditions the reaction would take place. Berthelot² found that no noteworthy action took place during the first few days in a solution containing sodium acetate and potassium permanganate. After three months he observed an appreciable reduction with the formation of carbonates. After a few hours' boiling the reduction was greatly promoted. This was especially so in the presence of a considerable amount of potassium hydroxide. A considerable reduction of the permanganate was observed after 10 hours of heating, and oxalic acid was found to be present. Lossen³ prepared a solution of potassium acetate, sodium hydroxide and potassium permanganate with the least amount of water and evaporated it to dryness. He heated the dried mass to a temperature at which the oxalate formed would not decompose and until the green color of the manganate had disappeared. The filtrate from the manganese dioxide on treatment with acetic acid and calcium chloride was found to contain oxalic acid. Denis⁴ found that aqueous solutions of acetates even in the presence of a very large amount of sodium or potassium hydroxide are unaffected by prolonged digestion with an excess of potassium permanganate. This investigator found only traces of manganese dioxide even after a solution of 1 g. of potassium acetate had been heated with 50 cc. of *N* potassium permanganate solution at 115–120° for 3 hours.

The lack of harmony in these results is not due to inaccurate observation, but rather to the fact that the experiments were obviously not carried out under like conditions of temperature, concentration of reacting materials

TABLE I
ANALYTICAL RESULTS

Calculated to basis of 0.1 mole KAc. Temp. 50°					
Alk. used G.	Oxalic obtained G.	KOH G.	KOH equiv. moles	Oxalic G.	Oxalic moles
14.62	0.517	15.4	0.274	0.544	0.006
28.18	0.586	29.6	0.526	0.617	0.007
55.95	0.677	58.9	1.05	0.712	0.008
112.0	0.889	118.0	2.10	0.935	0.011
170.8	1.021	179.0	3.19	1.07	0.012
Temp. 75°					
0.00	0.770	0.0	0.000	0.810	0.009
14.09	0.799	14.80	0.263	0.841	0.009
28.01	0.944	29.6	0.526	0.994	0.011
56.20	1.070	59.2	1.05	1.025	0.012
112.4	1.349	118.0	2.10	1.42	0.016
169.8	1.662	179.0	3.18	1.75	0.020

² Berthelot, *Ann. Spl.*, **6**, 183 (1868). Donath and Ditz, *J. prakt. Chem.*, [II] **60**, 573 (1899).

³ Lossen, *Ann.*, **148**, 174–176 (1868).

⁴ Denis, *Am. Chem. J.*, **38**, 568 (1907).

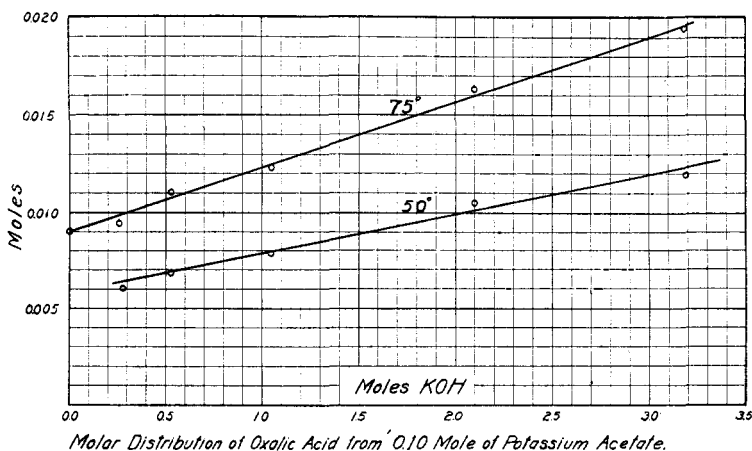
and time. That these three factors are important ones follows from a comparison of the results of these investigators with those given below. Our experiments were carried out essentially as follows. Thirty g. of potassium permanganate and the chosen weight of potassium hydroxide were dissolved in 950 cc. of water free from carbon dioxide. After this solution had attained the temperature of the thermostat, 9.3144 g. of potassium acetate dissolved in 50 cc. of water was then added to it. The reaction mixtures at 50° and 75° were stirred for 384 and 72 hours, respectively, and the unused potassium permanganate decomposed with sodium hypophosphite. The filtrate from the manganese dioxide was analyzed in each case for its oxalic acid content by the use of potassium permanganate in the usual way. The results are given in the foregoing table.

The filtrates from the reaction mixtures of high alkalinity contained large quantities of silicic acid which had to be removed by careful dehydration. That the white precipitate obtained with calcium acetate was actually calcium oxalate was conclusively proved by converting known quantities of this salt, dried at 100°, into calcium sulfate. The following results were obtained.

No.	CaC ₂ O ₄ ·H ₂ O G.	CaSO ₄ found G.	Calc. G.
1	0.2464	0.2296	0.2295
2	0.2550	0.2365	0.2375

Discussion

Our results show that both temperature and concentration of the potassium hydroxide have a marked effect on the yield of oxalic acid which may be obtained by the oxidation of potassium acetate. These facts are clearly set forth in Fig. 1. Since the yields of oxalic acid are small it is



obvious that the concentration of the permanganate is changed but very little. That acetates are not oxidized to oxalates in neutral solutions containing small concentrations of permanganate has been shown by the action of this reagent toward ethyl alcohol and acetaldehyde.⁵ In some unpublished experiments on propylene glycol this same fact has also been observed. The time employed for the experiments at 75° was approximated from that employed at 50° on the basis of the Ostwald rule in which we used a differential of 10°.

Summary

1. Potassium acetate may be oxidized to potassium oxalate with alkaline potassium permanganate under certain definite conditions.

2. The yield of oxalic acid is a function of the concentration of the reacting materials, the temperature and the duration of the experiment.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS,
NORTHWESTERN UNIVERSITY]

ORGANIC MERCURY COMPOUNDS PREPARED FROM ORTHO- CHLOROMERCURI-PARA-NITROBENZOYL CHLORIDE¹

BY FRANK C. WHITMORE AND EDMUND BURRUS MIDDLETON²

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Very few mercury derivatives of aromatic esters are known. These have been prepared by direct mercurization of the esters by mercuric acetate. Methyl benzoate gives mono- and dimercurated compounds, the structures of which have not been definitely established.³ *o*-Chloromercuribenzoic methyl ester has been obtained from methyl alcohol and sulfidomercuri-benzoyl chloride.⁴ The esters of *ortho*- and *para*-aminobenzoic acids and their mono- and di-alkyl derivatives give mono- and dimercurated compounds.⁵ Esters of salicylic acid react with mercuric acetate giving mono-mercurated compounds.⁶

Mercurated acid chlorides were unknown until recently, when *o*-chloromercuri-benzoyl chloride was prepared from thionyl chloride and the

¹ THIS JOURNAL, **41**, 1273, 1390 (1919).

² Presented at the Rochester Meeting of the American Chemical Society, April 1921.

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⁴ Schoeller and Schrauth, *Ber.*, **53**, 636 (1920).

⁵ Sachs, *ibid.*, **53**, 1741 (1920).

⁶ Schoeller and Hueter, *ibid.*, **47**, 1930 (1914). Schoeller, Schrauth and Liese, *ibid.*, **52** 1777 (1919). Ref. 3, p. 634.

⁶ Ref. 3, p. 639.