

Improved Method for Determination of 2,2-Dichloropropionic Acid in Chlorinated Propionic Acid by Use of Buffered Mercuric Nitrate Solution

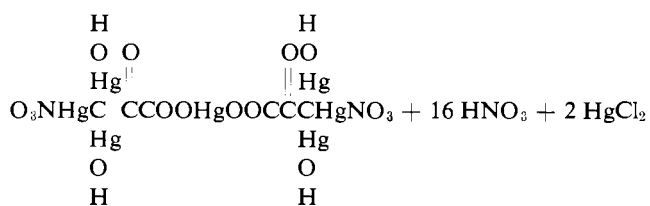
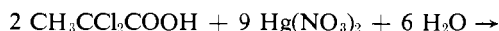
An improved procedure for the determination of 2,2-dichloropropionic acid in chlorinated propionic acid by reaction with mercuric nitrate has been developed. Conditions are established to produce one organic mercury compound almost exclusively which is reacted with aqueous potassium iodide to produce

potassium hydroxide. The stoichiometrical relationship is 1 mole of 2,2-dichloropropionic acid to 5 moles of potassium hydroxide; the base is titrated as a measure of the acid. Accuracy is achieved by calibration with a standard sample of 2,2-dichloropropionic acid.

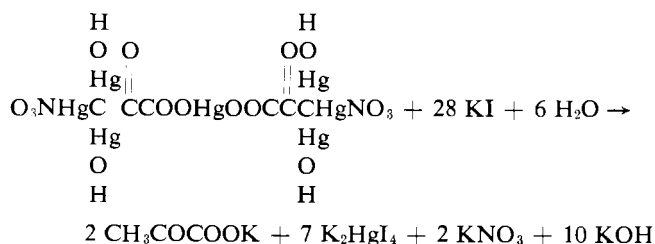
Analytical methods for 2,2-dichloropropionic acid in chlorinated propionic acid and for sodium salt of 2,2-dichloropropionic acid in the sodium salt of chlorinated propionic acid by use of mercuric nitrate solutions were published (Marquardt and Luce, 1959). The methods were capable of giving good analytical results, even though they were empirical. Recently further studies were made of the reactions of mercuric nitrate with 2,2-dichloropropionic acid. Conditions were established to produce only one organic mercury compound almost exclusively, and the chemistry of this reaction was elucidated. The result is a greatly improved procedure, based on a firm theoretical footing, for the determination of 2,2-dichloropropionic acid and of the sodium salt.

CHEMICAL REACTIONS USED FOR THE DETERMINATION OF 2,2-DICHLOROPROPIONIC ACID

A mercuric nitrate solution with a mercuric propionate-propionic acid buffer system suitable for either 2,2-dichloropropionic acid or the sodium salt is prepared that promotes the reaction of mercuric nitrate with 2,2-dichloropropionic acid to produce bis[bis(hydroxymercurio)(nitratomercurio)pyruvato] mercury almost exclusively, according to the following reaction.



The organic mercury compound is a mercarbide, a class of compounds in which three of the valences of a carbon atom are taken up by carbon-mercury bonds. Often a compound of this class is very stable, but in this case the mercarbide compound is reactive because the carbon atoms to which the mercury is attached are adjacent to carbonyl groups. Bis[bis(hydroxymercurio)(nitratomercurio)pyruvato] mercury reacts easily with aqueous potassium iodide to produce potassium hydroxide.



The stoichiometrical relationship shows that 1 mole of 2,2-dichloropropionic acid produces 5 moles of potassium hydroxide.

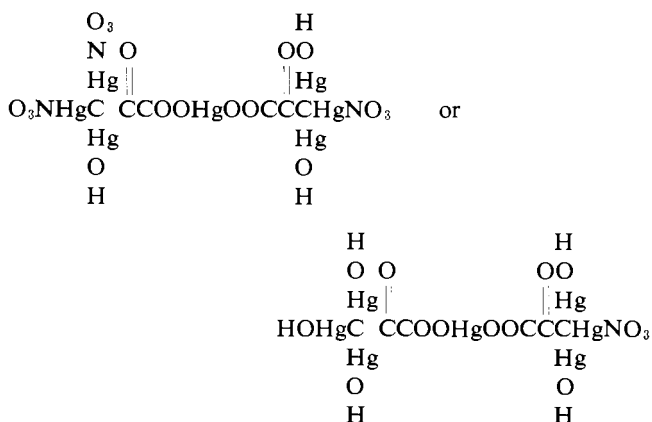
EXAMINATION OF BIS[BIS(HYDROXYMERCURIO)(NITRATOMERCURIO)PYRUVATO] MERCURY

The product of the reaction of mercuric nitrate with 2,2-dichloropropionic acid is a very insoluble cream-colored solid. The compound was analyzed for the elements and the results agree very closely with the theoretical values for the elements in bis[bis(hydroxymercurio)(nitratomercurio)pyruvato] mercury.

	Found, %	Theory, %
Carbon	4.05	4.08
Hydrogen	0.32	0.23
Nitrogen	1.65	1.59
Mercury	79.5	79.59
Oxygen (by difference)	14.48	14.51

The exact locations of the $-\text{HgOH}$ and $-\text{HgNO}_3$ groups in the molecule have not been proved. Considering the product to be bis[bis(hydroxymercurio)(nitratomercurio)pyruvato] mercury gives the stoichiometrical relationship between 2,2-dichloropropionic acid and potassium hydroxide found by experiment.

The reaction is not quite exclusive. For examples, depending on variations in the quality of preparations of mercuric nitrate solutions, various amounts of



may be produced with the main product, causing small changes in the amount of potassium hydroxide produced when the organic mercury product is reacted with aqueous potassium iodide. Therefore calibration of each preparation of mercuric nitrate solution is necessary for accurate determinations of 2,2-dichloropropionic acid.

DETERMINATION OF 2,2-DICHLOROPROPIONIC ACID AND SODIUM SALT OF 2,2-DICHLOROPROPIONIC ACID

Apparatus. Same as for the original procedure of Marquardt and Luce.

Reagents. Same as for the procedure of Marquardt and Luce, except that the mercuric nitrate solutions are replaced by one prepared as follows. Dissolve 150.0 g of ACS grade yellow mercuric oxide and 150.0 g of ACS grade cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in 450.0 ml of $3.000 \pm 0.003 N$ nitric acid and 40.0 ml of propionic acid (certified, Fisher Scientific Co., or equivalent). Dilute the solution to exactly 1 l. in a volumetric flask and mix. Filter the small amount of solids from the solution and add two drops of Dow Corning Antifoam B to the filtrate. Calibrate the mercuric nitrate solution according to the directions in "Calibration of the Mercuric Nitrate Solution."

2,2-DICHLOROPROPIONIC ACID. Analytical standard 2,2-dichloropropionic acid of 99+ % known purity by glc is available from the Sample Coordinator, Agricultural Department, The Dow Chemical Company, Midland, Mich. 48640

Calibration of the Mercuric Nitrate Solution. Pipet 100.0 ml of mercuric nitrate solution into a ball-jointed 250-ml Erlenmeyer flask. Add a weighed sample of the analytical standard containing 2.0 to 3.5 mequiv (0.06 to 0.10 g) of 2,2-dichloropropionic acid and some boiling chips to the solution.

Continue as in the procedure of Marquardt and Luce and calculate the factors for 2,2-dichloropropionic acid and for sodium salt of 2,2-dichloropropionic acid.

Procedure. For 2,2-dichloropropionic acid, pipet 100.0 ml of calibrated mercuric nitrate solution into a ball-jointed 250-ml Erlenmeyer flask. Add a weighed sample containing 1.5 to 4.0 mequiv (0.05 to 0.11 g) of 2,2-dichloropropionic acid and some boiling chips to the solution.

For sodium salt of 2,2-dichloropropionic acid, place a weighed sample containing 1.5 to 4.0 mequiv (0.05 to 0.13 g) of sodium salt in a ball jointed 250-ml Erlenmeyer flask. Pipet 100.0 ml of calibrated mercuric nitrate into the flask and add some boiling chips to the solution.

Continue as in the procedure of Marquardt and Luce and calculate the percent 2,2-dichloropropionic acid or sodium salt of 2,2-dichloropropionic acid.

Calculations. (A) CALCULATIONS OF THE 2,2-DICHLOROPROPIONIC ACID FACTOR AND THE SODIUM SALT FACTOR FOR CALIBRATION OF THE MERCURIC NITRATE SOLUTION,

$$\frac{A \times B}{C \times D} = E$$

$$\frac{164.951 \times E}{142.969} = F$$

(B) CALCULATIONS FOR 2,2-DICHLOROPROPIONIC ACID AND FOR SODIUM SALT OF 2,2-DICHLOROPROPIONIC ACID.

$$\frac{C \times D \times E \times 100}{\text{sample weight}} = \% \text{ 2,2-dichloropropionic acid}$$

$$\frac{C \times D \times F \times 100}{\text{sample weight}} = \% \text{ sodium salt of 2,2-dichloropropionic acid}$$

where

$$A = \frac{\text{percent}}{100} \text{ 2,2-dichloropropionic acid in the standard}$$

$$B = \text{sample weight of standard 2,2-dichloropropionic acid}$$

- C = ml of standard 0.1 N HCl solution
 D = factor for standard 0.1 N HCl solution
 E = factor for 2,2-dichloropropionic acid
 F = factor for sodium salt of 2,2-dichloropropionic acid.

Discussion. In addition to the topics discussed in the publication of Marquardt and Luce are the following. Cupric nitrate is added to the mercuric nitrate solution to promote the desired reaction of mercuric nitrate with 2,2-dichloropropionic acid. The mercuric nitrate solution contains a mercuric propionate-propionic acid buffer system. The nitric acid neutralizes 146.2 g of the 150.0 g of mercuric oxide, leaving 3.8 g to be neutralized by the excess propionic acid. The mequiv of 2,2-dichloropropionic acid and the sodium salt, based on one-fifth of the molecular weights in grams, are 0.0286 and 0.0330, respectively. The actual mequiv will be close to these values. Good analytical results are obtained when the titration is from 15 to 40 ml of standard 0.1 N hydrochloric acid; the method works best, however, when the titration is within the range of 20 ml to 35 ml of standard acid.

CAUTION! Do not use acetone for rinsing and drying glassware; acetone, containing a carbonyl group, will react with mercuric nitrate to give erroneous analytical results. Methanol may be used for rinsing and drying.

In the procedure of Marquardt and Luce, do not use more than 25 ml of potassium iodide solution from the wash bottle to wash the flask and funnel.

If it is ever necessary to analyze samples containing but a few percent of 2,2-dichloropropionic acid or sodium salt which would require extra large amounts of the samples in order to obtain at least 15-ml titrations with 0.1 N hydrochloric acid solution, a mercuric nitrate solution buffered at a higher pH should be used. Prepare this mercuric nitrate solution as follows.

Dissolve 150.0 g of ACS grade yellow mercuric oxide and 150.0 g of ACS grade cupric nitrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, in 450.0 ml of $3.000 \pm 0.003 N$ nitric acid and 40.0 ml of propionic acid (certified, Fisher Scientific Company, or equivalent). Add 150.0 ml of standard 1.00 N sodium hydroxide solution.

Table I. Analysis of Known Solutions of 2,2-Dichloropropionic Acid Containing Various Impurities

Impurity Added	% Added	% 2,2-Dichloropropionic Acid (Calculated)	% 2,2-Dichloropropionic Acid (Found)
None	86.46 86.46
$\text{CH}_3\text{CHClCOOH}$ (8.56% $\text{CH}_2\text{CCl}_2\text{COOH}$)	9.03	79.42	79.32 79.03
$\text{CH}_2\text{ClCCl}_2\text{COCl}$ (1.00% as $\text{CH}_2\text{CCl}_2\text{COOH}$)	11.12	76.96	76.96 76.75
CH_2ClCOOH	8.38	79.21	79.33 78.88
CHCl_2COOH	10.88	77.05	77.17 76.81
CCl_3COOH	8.68	78.96	77.75 77.71
CCl_3COOH	4.18	82.85	82.38 82.18
CCl_3COOH	1.52	85.14	84.99 84.93

Dilute the solution to exactly 1 l. in a volumetric flask. Filter the small amount of solids from the solution and add two drops of Dow Corning Antifoam B to the filtrate. Calibrate and use the mercuric nitrate solution according to the procedure. Analytical results for 2,2-dichloropropionic acid and sodium salt are valid even if the titrations are only 2 ml of 0.1 *N* hydrochloric acid solution. Since the analytical results are more erratic (of little consequence from a practical viewpoint for low concentrations of 2,2-dichloropropionic acid or salt), this solution is not recommended for use in analyzing high concentrations of the acid or salt.

ANALYTICAL DATA

A sample of chlorinated propionic acid, analyzed by use of a calibrated mercuric nitrate solution, was found to contain 86.46% 2,2-dichloropropionic acid. Known solutions were prepared with portions of this sample by the respective additions of various compounds that may be present as impurities: 2-chloropropionic acid (containing 8.56%, 2,2-dichloropropionic acid), 2,2,3-trichloropropionyl chloride (containing 1.00% 2,2-dichloropropionyl chloride as 2,2-dichloropropionic acid—pure 2,2,3-trichloropropionic acid was not available), chloroacetic acid, dichloroacetic acid, and trichloroacetic acid. None of these impurities except trichloroacetic acid gave any interference. Approximately 2% of trichloro-

acetic acid may be present before serious interference begins; since this acid has never been found to be present in chlorinated propionic acid in more than trace quantities, trichloroacetic acid can be considered not to be an interfering impurity. Pyruvic acid, of course, will interfere if present. The analytical results are shown in Table I.

A sample of distilled chlorinated propionic acid was repeatedly analyzed for 2,2-dichloropropionic acid. The results obtained were 87.43, 87.09, 87.17, 87.16, 87.28, 87.09, 87.40, 87.26, 87.52, 87.20, 87.06, and 87.33%. The standard deviation is 0.15%.

Likewise a sample of the sodium salt of 2,2-dichloropropionic acid was repeatedly analyzed for the sodium salt of the acid. The results obtained were 83.85, 83.95, 84.08, 84.02, 83.82, 83.70, 83.94, 83.75, 83.71, 84.06, 84.02, and 84.28%. The standard deviation is 0.17%.

LITERATURE CITED

Marquardt, R. P., Luce, E. N., *Anal. Chem.* **31**, 418 (1959).

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Received for review April 13, 1970. Accepted September 28, 1970.