

Hydrolysis of Aqueous Solutions of Sodium 2,2-Dichloropropionate under Self-Induced Alkaline Conditions

Fred S. Tanaka* and Ronald G. Wien

Aqueous solutions of sodium 2,2-dichloropropionate were previously reported as having an approximate pH of 5 to 6. The data obtained in this study show that freshly prepared solutions of greater than about 0.9 *m* concentration exhibit a basic pH. Upon standing, however, these salt solutions become acidic due to the hydrolysis of the

2,2-dichloropropionate to yield pyruvate and hydrochloric acid. The approximate pH of the sodium 2,2-dichloropropionate solutions is estimated at different concentrations, and the rates of pH change due to hydrolysis are reported for a dilute, intermediate, and high concentration of material under mildly alkaline conditions.

The herbicide 2,2-dichloropropionic acid (dalapon) is generally applied as the sodium salt to control grasses in a variety of crops and also in noncrop conditions such as ditch banks and aquatic weeds. Sodium 2,2-dichloropropionate (sodium dalapon) is known to hydrolyze in the presence of water (Paynter *et al.*, 1960; Smith and Dyer, 1961; Smith *et al.*, 1953), and the products of hydrolysis are pyruvic acid and hydrochloric acid (Leasure, 1964). To our knowledge, however, the initial rapid rate of hydrolysis of concentrated solutions of sodium 2,2-dichloropropionate has not been reported. Our interest in the pH and the hydrolysis of sodium dalapon was initiated when we found that it was not possible to maintain an aqueous solution of this material at an approximate pH of 9 for several days.

EXPERIMENTAL SECTION

Technical grade 2,2-dichloropropionic acid was supplied by the Dow Chemical Company, Midland, Mich. Sodium hydride (58% dispersion in mineral oil) was purchased from the Ventron Corporation. Vacuum distillations were performed on a No. A-382 spinning band column (Nester/Faust Mfg. Corp.). Melting point measurements were accomplished on a Thomas-Hoover capillary apparatus and were reported uncorrected. The samples were stirred into solution on a Vortex-Genie mixer.

Gas-liquid chromatography was performed on a Barber-Coleman 5000 chromatograph equipped with a flame ionization detector. A column of 15% SE-30 on Gas Chrom Q (60 to 80 mesh) was employed and operated at 90° with a nitrogen flow rate of 85 ml/min. The 2,2-dichloropropionic acid was derivatized to the methyl ester prior to gas chromatography using the methanol-sulfuric acid method reported by Woolson and Harris (1967). Estimation of product yield was achieved by comparison of peak height with values on a standard curve prepared from samples of known concentration.

A Corning Model 10 pH meter equipped with a Corning No. 476050 single-probe electrode was used to measure pH. All readings were observed on the expanded scale except those under pH 5.5 and those exceeding pH 8.5. Beckman Buffer No. 3007 with a pH of 7.00 ± 0.03 at a temperature of 25 ± 5° was used for the calibration of the instrument.

Triply distilled water was used throughout these experiments. For the preparation of the distilled water, standard laboratory procedures were used for the first two distillations, and the final distillation was performed from a

solution of basic potassium permanganate. A pH of 6.41 was observed for this distilled water.

2,2-Dichloropropionic Acid. Technical grade 2,2-dichloropropionic acid was purified by three successive vacuum distillations. The first fractionation was performed in a standard vacuum distillation apparatus equipped with a Claisen distillation head. The following two distillations were accomplished on a spinning band column with the reflux ratio set at 10:1. Each distillation was fractionated to provide maximum sample enrichment. The boiling point of the purified material was 106° at 35 mm pressure. Purity of the 2,2-dichloropropionic acid was estimated as greater than 98% by gas-liquid chromatography.

Anhydrous Sodium 2,2-Dichloropropionate. A 100-ml three-necked flask was equipped with addition funnel, mechanical stirrer, and reflux condenser with drying tube. The flask was charged with 4 g (0.10 mol) of sodium hydride (58% dispersion in mineral oil) and 25 ml of anhydrous tetrahydrofuran (THF). Then 11 ml (0.11 mol) of 2,2-dichloropropionic acid was dissolved in 10 ml of THF in the addition funnel. The acid solution was slowly added with vigorous stirring to the sodium hydride. Following addition of the acid, 10 ml of benzene was added, and the reaction mixture was stirred for 1 hr. The precipitated product was isolated by vacuum filtration and washed with hexane. The sodium 2,2-dichloropropionate was redissolved in warm THF, filtered, and allowed to recrystallize. The recrystallized product was again separated by vacuum filtration and washed with hexane. To remove all volatile impurities, this material was transferred into a heavy-walled vacuum bottle and placed under vacuum (*ca.* 0.3 Torr) for 3 days with occasional flushing of the vessel with dry air. The product was a white flocculent solid which melted sharply with decomposition to yield a medium brown liquid. An average melting point of 195° was obtained in agreement with the 193–197° melting point range reported in the literature (Kearney *et al.*, 1965). The nmr spectra showed only a singlet at 2.6 ppm (–CH₃ group) in acetone-*d*₆.

Estimation of Solution pH. For a typical experiment, 0.5 g of sodium 2,2-dichloropropionate was transferred into a 15 × 125 mm test tube. One milliliter of distilled water was pipetted into the test tube to prepare a 3.0 molal (*m*) solution. The mixture was vigorously agitated on a vortex stirrer to effect solution; this required approximately 5 sec. The electrode was immediately immersed into the solution, and the pH was observed after the electrode and solution reached equilibrium. Equilibration of the electrode was usually achieved in about 45 sec, and during this period the solution was gently agitated.

All pH measurements were determined at approximately 23°. The pH values given in Figure 1 were an average value for three to seven observations. Only one measurement was determined for a 5.4 *m* solution which required

* Plant Science Research Division, Agricultural Research Service, U. S. Department of Agriculture, Metabolism and Radiation Research Laboratory, Fargo, North Dakota 58102.

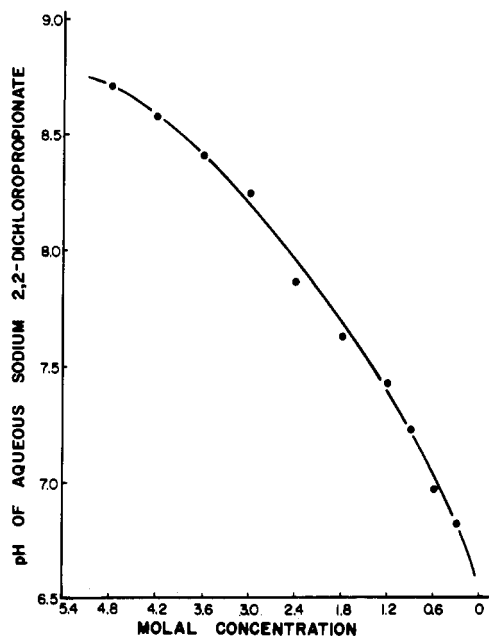


Figure 1. The approximate pH of aqueous sodium 2,2-dichloropropionate solutions as a function of concentration.

approximately 3 to 4 min of mixing time to dissolve the material. A pH value of 8.4 was obtained for this solution.

Rates of pH Change. Dilute basic salt solutions of 0.25 *m* concentration were prepared in triplicate by dissolving 3.6 g of 2,2-dichloropropionic acid in 100 ml of distilled water with pH adjustment to 9.7, employing 0.1 *M* sodium hydroxide. The pH measurements were obtained at various daily intervals (Table I).

Duplicate samples of 2.4 and 4.8 *m* concentration of sodium 2,2-dichloropropionate were prepared for the time course study. Preparation and measurement of samples were identical to those previously described for a typical experiment. The pH of the dalapon salt solutions was measured at various intervals of minutes (Figure 2).

Hydrolysis Study. The hydrolysis products of sodium 2,2-dichloropropionate were identified as pyruvic acid, hydrochloric acid, and their neutralized salts. Pyruvic acid was isolated as the 2,4-dinitrophenylhydrazone derivative and characterized by ir, nmr, and mass spectrometry. The chloride ion was characterized as its silver salt.

Hydrolysis was followed by titration of the chloride ion produced (Fischer, 1961) and by estimation of the residual sodium dalapon by gas-liquid chromatography. The results by both methods were in agreement; however, the gas chromatographic method appeared to result in slightly greater precision.

For a quantitative measure of hydrolysis in moderate and high concentrated samples, duplicate samples of 2.4

Table I. Change in pH of 0.25 *m* Aqueous Solutions of Sodium 2,2-Dichloropropionate Adjusted to pH 9.7

Elapsed time, days	pH
0	9.7
1	9.5
2	8.9
3	8.0
4	6.9
5	6.2
6	5.5
7	5.0
8	4.7
16	3.9
30	3.6
40	3.4

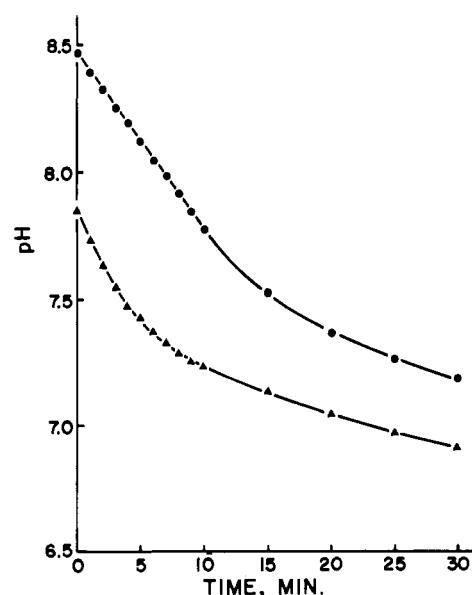


Figure 2. The rate of hydroxide ion depletion from freshly prepared aqueous solutions of sodium 2,2-dichloropropionate; ●, 4.8 *m*; ▲, 2.4 *m*.

and 4.8 *m* solutions of sodium dalapon were prepared. After effecting solution, an aliquot was immediately removed to estimate the concentration at zero time. A second aliquot was removed and analyzed 30 min after zero time. The amount of sodium dalapon remaining after 30 min was estimated as 96.5% of the initial concentration for both the 2.4 and 4.8 *m* solutions. These samples were then allowed to stand at room temperature (*ca.* 23°) for 14 days. After the 14-day period, the pH's of the solutions were 3.4 and 4.0 for the 2.4 and 4.8 *m* solutions, respectively. The concentration of sodium dalapon remaining in the 2.4 *m* solution was 94.5% and that of the 4.8 *m* solution was 95.0% of the initial value.

RESULTS AND DISCUSSION

A pH range of 5 to 5.6 was reported by Nex and Swezey (1954) for 5% aqueous solutions of sodium 2,2-dichloropropionate (sodium dalapon). According to Kearney *et al.* (1965), pH values of 5.7 and 6.0 were indicated for 1 and 50% solutions, respectively. The ionization constant (K_a) for 2,2-dichloropropionic acid was estimated as 2.94×10^{-2} (Foy, 1969). Therefore, the expected solvation and ionization of sodium dalapon in aqueous solution is as follows.



Thus, sodium dalapon would be expected to exhibit the properties of a salt of a strong base and a weak acid. At high concentration (*i.e.*, 50% solution) the equilibrium between solvated salt and free acid should be shifted in the direction of the unionized acid to such an extent as to yield a solution of basic pH. In Figure 1, pH is shown as a function of concentration, and pH values of 6.8 to 8.7 are observed for sodium dalapon solutions of 0.3 to 4.8 *m* concentration. A 3.8 *m* concentration is equivalent to a 50% (w/v) solution using 1.2987 g/ml (Kearney *et al.*, 1965) as the density. As expected, the higher concentrations of sodium dalapon do exhibit a pH greater than neutrality; but as the concentration is decreased, the equilibrium is shifted in favor of the ionized acid. Therefore, the dilute sodium dalapon solutions approach the pH of the solvent.

The pH values in Figure 1 which are measured at high sodium dalapon concentration are higher than would be predicted from simple pH calculation. Since high salt

concentrations can cause large deviations in activity coefficients of solvated ions in solution, these multiple interactions and deviations in many cases are responsible for solutions becoming ill-defined, complex systems. Therefore, from our pH studies it is not possible to clearly define the reason for the high pH values observed with increased concentration. However, the fact remains that these solutions do yield a basic pH at high concentration, and basic solutions enhance the rate of hydrolytic decomposition of the dalapon salt. Apparently, as the concentration increases, hydrolysis occurs at a rapid enough rate to quickly depress the pH of the solution. Therefore, the pH of solutions at high concentration is reduced below its true value before an accurate measurement can be obtained. An attempt was made to measure the pH of a 5.4 *m* solution; however, several minutes of stirring were required to effect solution. Consequently, decomposition reduced the pH to 8.4, which is less than that observed for the 4.8 *m* solution.

To examine the rate of pH change of dilute solutions of sodium dalapon at a basicity similar to the concentrated samples, basic solutions of 0.25 *m* concentration were prepared by adjusting the pH to 9.7 with sodium hydroxide. The rate of pH change in Table I shows that dilute aqueous solutions of sodium dalapon are only slowly hydrolyzed under mildly basic conditions. Therefore, dilute samples may possibly be utilized under mildly alkaline conditions such as in a basic buffered media for short-term experiments. However, loss of material by hydrolysis will be great enough under extended periods that long-term studies under alkaline conditions should be avoided.

The decomposition of sodium dalapon induced by the hydroxide ion generated from solvolysis of the dalapon salt in aqueous solution was examined. The 2.4 and 4.8 *m* concentrations were chosen to reflect the behavior of the intermediate and highly concentrated solutions. The rates of pH change with respect to time are given in Figure 2. These values are again only an approximate pH of the sodium dalapon solutions, since hydrolysis was occurring prior to sample measurement. However, the important factor observed here is the rate of pH change under basic conditions. Initial change in pH is rapid with changes of 0.07 to 0.10 pH units/min in the basic solutions. As the hydroxide ion is consumed, the rate of hydrolysis decreases. After 30 min the 2.4 and 4.8 *m* solutions are reduced to pH values of 6.9 and 7.2, respectively. This reduction in pH represents a loss of 3.5% of the initial sodium dalapon in both cases. These samples were then allowed to stand at room temperature for 14 days. At the end of this period, the 2.4 and 4.8 *m* solutions exhibited pH values of 3.4 and 4.0, respectively. The loss of material after 14 days was estimated to be 5.4% for the 2.4 *m* concentration and 5.0% for the 4.8 *m* solution.

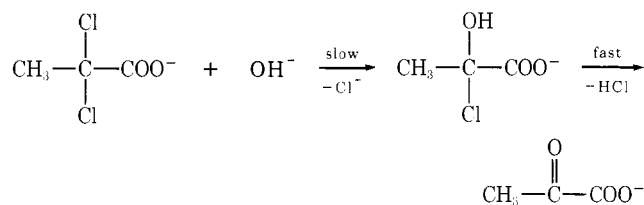
The data for the 4.8 *m* solution reveal that from time 0 to 30 min there is a change of 1.3 pH units, which represents a loss of 3.5% of the parent material. On the other hand, after 14 days there is an additional change of 3.2 pH units, which represents a loss of only 1.5% of the sodium dalapon after the initial 30-min period. More material is hydrolyzed in the initial 30-min period, even though a smaller change in pH occurs. This results from the fact that hydroxide ion is continuously being generated to initiate further reaction at the same time it is being consumed. When sodium dalapon is hydrolyzed to sodium pyruvate, a mole of hydrochloric acid is produced for each mole of hydroxide ion consumed; thus the solution eventually becomes acidic. Once the solution is acid, neutralization of the hydroxide ion becomes the favored reaction. Therefore, under mildly acidic conditions, only a small loss of parent material is observed.

The plot of pH *vs.* time for the 4.8 *m* concentration in Figure 2 reveals a linear relationship for approximately 10 min. At about pH 7.7, however, the curve begins to de-

viate from linearity. Under the condition of high dalapon salt concentration, the rate of hydrolysis is dependent only on the concentration of hydroxide ion (Frost and Pearson, 1961). Therefore, the hydroxide ion consumption appears to follow pseudo-first-order kinetics with an overall rate constant of *k*. Based on the relationship $\text{pH} = -kt/2.303 + \text{pH}_0$ (Fahmy *et al.*, 1972), where pH_0 is the initial pH and *t* is the time in minutes, a value for *k* can be calculated where a linear relationship with respect to pH and time is observed. Thus, from the slope of the curve, the value of *k* for the loss of hydroxide ion for the 4.8 *m* solution is estimated as 0.16 min^{-1} . Under basic conditions, the conversion of 1 mol of sodium dalapon to sodium pyruvate requires the consumption of 2 mol of hydroxide ion. Therefore, the formation of sodium pyruvate should follow the same kinetics as the consumption of hydroxide ion; however, the rate will only be half as great. Apparently, hydroxide ion is initially consumed more rapidly than it can be generated; therefore, the pH falls quickly with loss of hydroxide ion obeying first-order kinetics until pH 7.7 is attained. At this pH the generation of hydroxide ion by equilibrium shift again becomes significant, and the value of *k* is no longer valid.

Examination of the 2.4 *m* curve in the same manner as the 4.8 *m* data also reveals a linear relationship with respect to pH and time. This curve, however, only remains linear for about 3.5 min, whereupon a pH of 7.5 is attained. The rate constant (*k*) for the 2.4 *m* concentration is calculated as 0.23 min^{-1} , and this constant is valid to an approximate pH of 7.5. The difference observed between the 2.4 and 4.8 *m* rate constants could stem from initial differences in hydroxide ion concentration as well as from differences in ionic strength effected by the two dalapon salt concentrations. Here again, however, it is difficult to define these solutions at high ionic strength, and one can only speculate that significant deviations in activity coefficients or other factors peculiar to solutions of high ionic strength are responsible for these rate differences.

The base-induced hydrolysis of 2,2-dichloropropionate probably involves the initial formation of the unstable 2-chloro-2-hydroxypropionate intermediate which, in turn, eliminates hydrochloric acid to yield pyruvate, as shown below.



In support of this reaction sequence, Smith has reported by private communication in the review by Kearney *et al.* (1965) that 2-chloro-2-hydroxypropionic acid was prepared, and this material rapidly decomposed to yield pyruvic acid.

SUMMARY AND CONCLUSION

The two factors which have the greatest influence on the hydrolysis of aqueous sodium dalapon solutions are the concentration and the storage time. Since initial hydrolysis occurs at a fairly rapid rate at intermediate to high concentrations, only dilute solutions of sodium dalapon should be employed for experimental study if hydrolysis is to be minimized. In the preparation of sodium dalapon, neutralization of dilute 2,2-dichloropropionic acid with aqueous sodium hydroxide followed by evaporation will result in considerable decomposition of the acid to sodium pyruvate (Melnikov, 1971). Thin-layer chromatography of radioactive dalapon in aqueous solvent systems

containing inorganic base may also yield pyruvic acid as a hydrolytic byproduct. Furthermore, the storage of concentrated aqueous solutions of sodium dalapon prior to application will necessitate more material than generally required to obtain a desired result. The preparation of concentrated stock solutions will result in at least an initial 3 to 5% loss of material by hydrolysis and more upon storage. Therefore, stock solutions at high concentration which are diluted prior to application should not be prepared and stored for long periods (Melnikov, 1971).

It appears that sodium dalapon solutions with concentrations greater than about 0.9 *m* form basic solutions when freshly prepared (Figure 1). Upon standing, however, these solutions become acidic from the hydrochloric acid released by the decomposition of the dalapon salt. Therefore, the pH value of 6.0 reported for a 50% solution must be the observed pH for sodium dalapon and its hydrolytic byproducts rather than sodium dalapon alone. Although the quantity of material lost through hydrolysis to reduce the hydroxide ion concentration to an acidic pH is only 3 to 4%, this loss may become significant for certain material balance studies.

The pH values have been reported here for sodium dalapon solutions with respect to different concentrations. These values should not be considered as the true pH of the solution due to hydrolysis prior to measurement. The

results may be used, however, as a general guideline to indicate the approximate pH expected for a solution of given concentration.

LITERATURE CITED

- Fahmy, M. A. H., Khasawinah, A., Fukuto, T. R., *J. Org. Chem.* **37**, 617 (1972).
 Fischer, R. B., "Quantitative Chemical Analysis," W. B. Saunders Company, Philadelphia, Pa., 1961, p 286.
 Foy, C. L., "Degradation of Herbicides," Kearney, P. C., Kaufman, D. D., Ed., Marcel-Dekker, New York, N. Y., 1969, pp 207-253.
 Frost, A. A., Pearson, R. G., "Kinetics and Mechanism," Wiley, New York, N. Y., 1961, p 11.
 Kearney, P. C., Harris, C. I., Kaufman, D. D., Sheets, T. J., "Advances in Pest Control Research," Metcalf, R. L., Ed., Wiley, New York, N. Y., 1965, pp 1-30.
 Leasure, J. K., *J. Agr. Food Chem.* **12**, 40 (1964).
 Melnikov, N. N., *Residue Rev.* **36**, 121 (1971).
 Nex, R. W., Swezey, A. W., *Weeds* **3**, 241 (1954).
 Paynter, O. E., Tusing, T. W., McCollister, D. D., Rowe, V. K., *J. Agr. Food Chem.* **8**, 47 (1960).
 Smith, G. N., Dyer, D. L., *J. Agr. Food Chem.* **9**, 155 (1961).
 Smith, G. N., Getzendaner, M. E., Kutschinski, A. H., *J. Agr. Food Chem.* **5**, 675 (1953).
 Woolson, E. A., Harris, C. I., *Weeds* **15**, 168 (1967).

Received for review June 26, 1972. Accepted January 3, 1972. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U. S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

The *p*-Value Approach to Quantitative Liquid-Liquid Extraction of Pesticides and Herbicides from Water. 2. Selection of Water:Solvent Ratios and Number of Extractions

Irwin H. Suffet

The general goal of aqueous pesticide residue analysis is the recovery of 100% of a pesticide and its degradation products for qualitative and quantitative analysis. The *p*-value concept has previously been used to determine the pH and solvent to approach 100% pesticide recovery. In this paper, equations are developed from liquid-liquid extraction theory for the number of extractions and water:solvent ratios for maximum recovery for typical *p*-values. A computer program analysis of the equations developed indicates that

a pesticide which has a *p*-value of ≥ 0.90 in an aqueous solvent system can be extracted from the aqueous phase with 95% recovery in ≤ 5 successive extractions of ≥ 50 ml with a total volume ≤ 500 ml of solvent. The equations were successfully tested with serial extraction of 2,4-D by separatory funnel and vortex stirring extraction procedures. The contribution to the total error of initial LLE step was estimated to be less than 20% for a four-step serial extraction.

Aqueous pesticide residue analysis is concerned with the reproducible minimum detectable concentration of a given analytical procedure (Brown and Nishioka, 1967; Faust and Suffet, 1969; Nicholson, 1967). The general goal of aqueous pesticide residue analysis is to recover 100% of a pesticide and its metabolites, if present, for quantitation and/or identification. Some quantity of a compound is lost during each analytical step (*i.e.*, extraction, concentration, clean-up, etc.) of a residue method. It is necessary to minimize these losses.

The general practice is to report recovery efficiencies by fortification techniques, that is, the addition of a known quantity of a pesticide to water in a laboratory test prior to processing the sample through each step of the analyti-

cal procedure. Fortification techniques provide data only on the theoretical recovery efficiency of the total analytical procedure and not on the liquid-liquid extraction (LLE) step alone.

The question remains: do the percent recoveries from the fortification procedure represent the actual recovery efficiencies from field samples? The pitfalls of the fortification procedure have been discussed for plant and soil pesticide residues (Gunther, 1962; Wheeler and Frear, 1966). Hermann and Post (1968) have demonstrated the extraction of model pollutants from distilled water to be different than their extraction from natural water. Gunther (1962) concluded that the fortification process is "illusory except in a few instances." A completely homogeneous system such as a true solution may approach actual field recovery. However, field samples are "weathered" (subject to physical, chemical, and metabolic transformations) and may be in aggregate or molecular form in or on

Department of Chemistry, Environmental Studies Institute, Drexel University, Philadelphia, Pennsylvania 19104.