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Authors

Tashinian, Vazken H.
Baker, Mary Jane
Koch, Charles W.

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February 16, 1956

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Vazken H. Tashinian and Mary Jane Baker

Department of Chemistry and Chemical Engineering
University of California, Berkeley, California

Charles W. Koch

Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

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ABSTRACT

Samples to be analyzed for methyl groups attached to carbon were digested with the chromic acid-sulfuric acid mixture in sealed tubes, which were heated in a rocking furnace. A jacketed distillation apparatus was used to aid in distilling the acetic acid produced from the reaction mixture. The distillation apparatus eliminated carry-over of sulfuric acid spray and reduced the time required for distillation when the jacketing substance boiled at a temperature approximating the boiling point of acetic acid. Diagrams of the apparatus used are included. Typical data are listed to show that acetic acid is produced quantitatively from several low-boiling aliphatic compounds. Data are also included to show that acetic acid is not obtained quantitatively from low-molecular-weight aliphatic amines. Three relatively complex compounds were investigated, by employing the Kuhn-Roth oxidation mixture and the increased amount of sulfuric acid proposed by Ginger. The results do not show one reaction mixture to be clearly superior. However, they do suggest that prolonged digestion with the lesser amount of sulfuric acid is more likely to produce the optimum amount of acetic acid.

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Department of Chemistry and Chemical Engineering
University of California, Berkeley, California

Charles W. Koch

Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

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INTRODUCTION

The Kuhn-Roth method³ for the determination of terminal methyl groups is based upon the oxidation of hydrocarbon chains, $\text{CH}_3-\overset{\curvearrowright}{\text{C}}-$, with a chromic acid-sulfuric acid mixture. Under the conditions employed, the oxidation of acetic acid by the reaction mixture is relatively slow compared with the oxidation of the sample to acetic acid.

Ginger² reported that the theoretical amount of acetic acid is approached more nearly if the sample is first dissolved in 2 ml of concentrated sulfuric acid (rather than the 1 ml employed in the Kuhn-Roth procedure). This indicates that, in the time allotted for digestion, the Kuhn-Roth reaction mixture does not oxidize all of the fatty acid to acetic acid, or that the increased sulfuric acid concentration used by Ginger actually favors the formation of acetic acid in the oxidation process. Of these two possibilities, the former seems more reasonable.

Campbell and Morton¹ showed that they could not obtain quantitative yields of acetic acid when gem-dimethyl or tertiary butyl groups were present in the compound studied. They also stated that low results could not be attributed to the formation of acetone in the oxidation step, since samples of acetone and mesityl oxide each produced approximately three-fourths of the theoretically expected amount of acetic acid. Although Campbell and Morton did demonstrate that the major portion of each of these samples was oxidized to acetic acid, the missing one-fourth in each instance is unexplained. For acetone, the loss must be due either to volatility or to stability of the molecule itself. In mesityl oxide the problem is complicated

further by the presence of a $(\text{CH}_3)_2-\overset{\curvearrowright}{\text{C}}$ group, for which Campbell and Morton obtained recoveries of the order of 75% to 85%. However, loss of sample by volatility should have been reduced by use of this higher-boiling substance. The fact that the same relative amount of acetic acid is produced in the oxidation of mesityl oxide as of acetone tends to support the argument for the stability of some nonacidic fragment in the reaction mixture.

Because of the uncertainty associated with volatilization from the reaction mixture of low-molecular-weight organic compounds during the refluxing step, all samples in the work reported here were digested in sealed tubes. Also, to ensure mixing of a gaseous organic compound and the sulfuric acid-chromic acid solution, digestions were carried out in a rocking furnace.

The conventional apparatus of Kuhn and Roth for the distillation of acetic acid was not employed in this work, for two reasons. First, it is our experience, too frequently, that the distillate contains appreciable amounts of sulfate ion. Also it is desirable to shorten the distillation time, and this is accomplished by jacketing the distilling flask at a temperature that approximates the boiling point of acetic acid.

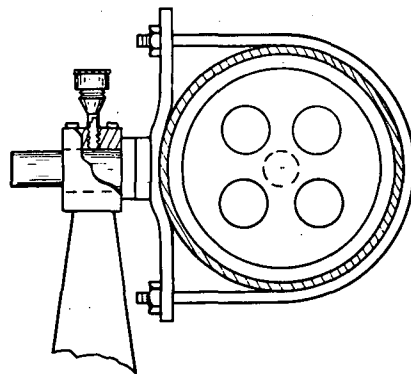
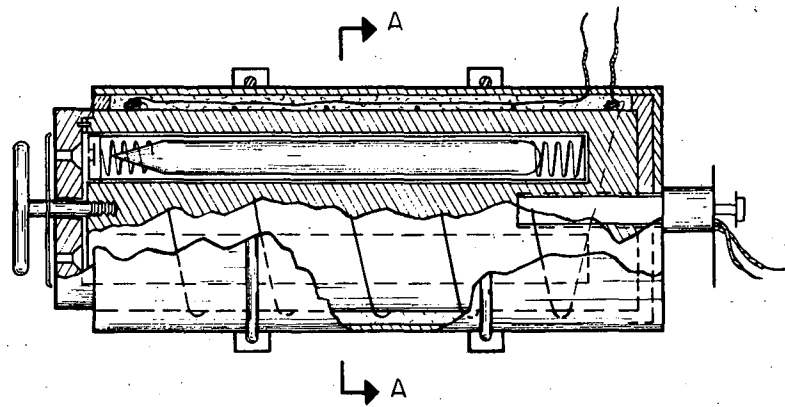
APPARATUS

Rocking Furnace

The furnace shown in Fig. 1 is constructed so that it rocks through an angle of 45° . It is driven by a Bodine Electric Co. 1/6-hp Type NSI-55RH motor, which runs at 38 rpm. The furnace is constructed from a 12-inch length of 4-inch-diameter dural. Four 10-inch holes, each 1-1/8 inch in diameter, are bored in the block. The cover is drilled so that each compartment has an outlet to the air, and a baffle is placed between the cover and the handle to protect the operator should one of the tubes break. A 1/4-inch pin on the face of the furnace, which fits into a hole in the cover, centers each vent over a compartment. The opposite end of the dural block is drilled to contain a Fenwal thermoswitch which can be controlled over the temperature range 110° to 205°C within $\pm 0.5^{\circ}\text{C}$. Two rings made from half-inch transite are used to center the dural block in an outer steel tube. The base ring is countersunk as shown in the figure. The two rings are slipped onto the dural block, and in each case held in place by means of three countersunk screws. The walls of the dural block are covered with asbestos paper and wrapped with 30 feet of 22-gauge chromel wire. The wire is fastened securely to two 1/4-inch transite pins mounted in the side of the dural block as shown in the figure. The chromel wire then is covered with asbestos rope and the unit is inserted into the steel tube, which is 4.75 inches in outside diameter and has a 1/16-inch wall thickness. The steel tube is fastened to each transite ring with screws. The furnace is attached to a rocking arm and mounted on a stand by means of a bearing as shown in Fig. 1, Section A-A.

Sealed-Tube Container

The container shown in Fig. 2 is made of 1-inch-diameter steel tubing having a 3/32-inch wall thickness, and is approximately 10 inches long. Its length is adjusted to fit into the furnace compartment so that it will not slide when the furnace is rocking. The cap contains a baffle as indicated in Fig. 1 as a further protection to the operator if a sealed tube should break. Coils of wire are inserted before and after the sealed tube to prevent breakage while the furnace is rocking, and also to allow variation in the length of the



SECTION A-A

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Fig. 1 Rocking furnace used for digestion of samples.



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Fig. 2. Steel casing and cover containing sealed tube to be placed in rocking furnace.

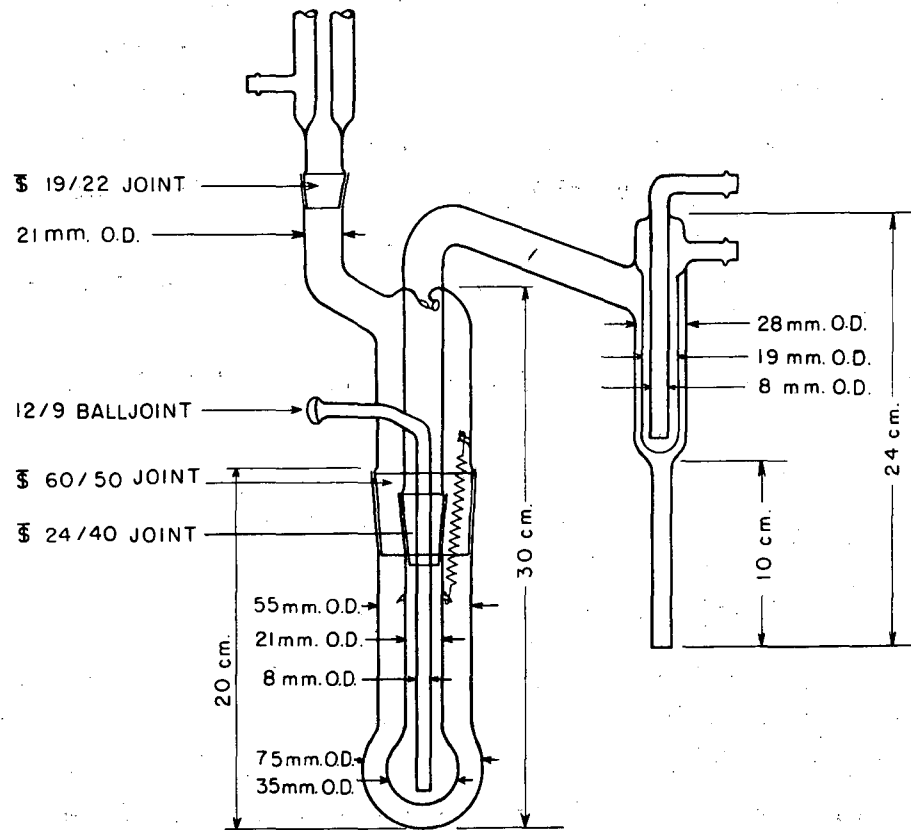
tube. The sealed tubes are made from 18-mm o. d. Pyrex tubing, and may vary from 6 to 9 inches in length.

Distillation Apparatus

The distillation apparatus employed for the work reported in this paper is shown in Fig. 3. Its use completely eliminates carry-over of sulfuric acid spray during distillation, and decreases the time necessary to obtain quantitative distillation of acetic acid. This apparatus permits jacketing the distilling flask at a temperature above that of the entering steam, thus increasing the rate of distillation of acetic acid.

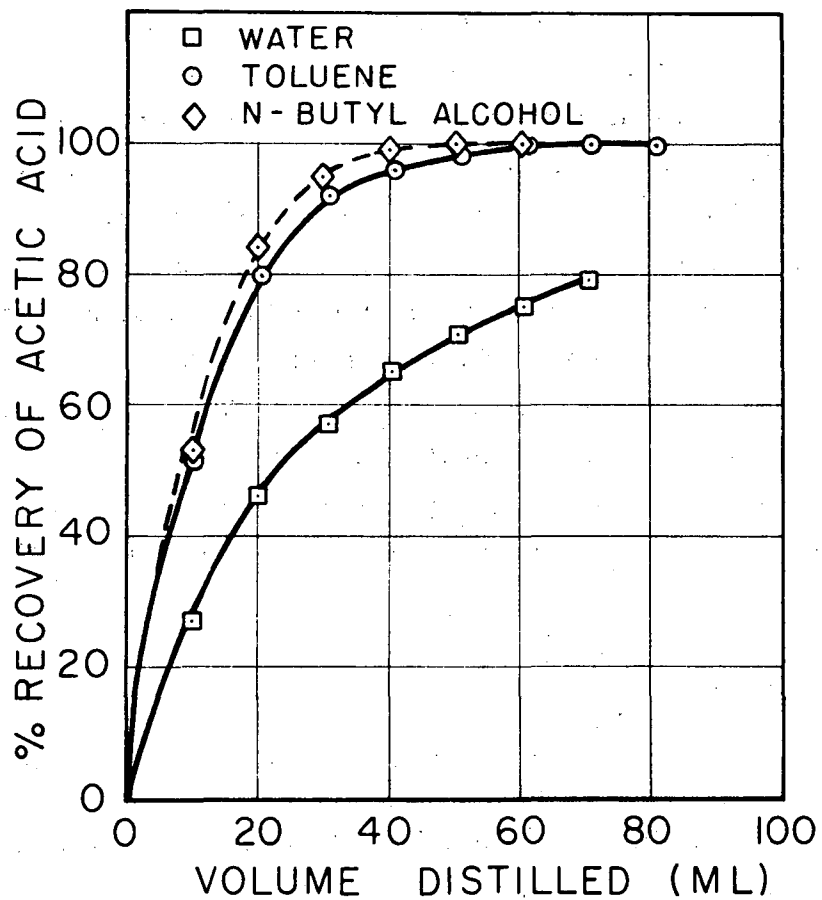
PROCEDURE

The oxidation mixtures employed for the experiments in this paper all contained 4 ml of 5 N chromic acid. The hydrogen ion concentration was varied, however, and in each set of experiments the amount of acid employed is specified together with the results. A sample sufficiently large to yield 0.05 to 0.08 millimole of acetic acid was employed for these determinations. When the sample to be analyzed was a solid it was weighed into the pyrex tube, and the oxidation mixture was added and the tube sealed. When the sample was a liquid having a low partial pressure so that it could be handled in air, it was weighed into a boat. The boat and sample were transferred to the oxidation mixture in the pyrex tube and the tube was sealed. If the sample was a liquid with a high vapor pressure, it was weighed in a capillary tube, the tube was dropped into the reaction mixture in the pyrex tube, and the tube was sealed. If the boiling point of the sample was greater than 100°C it was expelled from the capillary prior to the digestion period. The sealed tube was carefully tilted to leave the capillary suspended on the wall of the vessel free of the oxidation mixture, and the tube was warmed gently in the immediate vicinity of the sample until the liquid was expelled. The tube was righted rapidly to draw some of the oxidation mixture into the capillary. The sealed tube was then placed in the steel container shown in Fig. 2, which was in turn inserted into the rocking furnace at the desired temperature and the sample was heated for the required period of time. Prior to opening the sealed tube, the tip was heated to drive the liquid from it and



MU-11079

Fig. 3. Jacketed apparatus for the distillation of acetic acid.



MU-11080

Fig. 4. Curves showing the effect of jacket temperature on the rate of distillation of 0.05 mmole of acetic acid from a solution containing 4 ml of 5 N chromic acid, 1 ml of concentrated sulfuric acid, and 5 ml of water.

$\Delta F_{298^\circ K}$ per mole of acetic acid is -279 kcal. Even with this very large value for the free energy favoring the oxidation, it was found that the rate of loss of acetic acid during digestion was slow. After a 4-hour digestion period at $120^\circ C$ in 0.1 M $Cr_2O_7^{--}$, 96% of the acetic acid was recovered from a solution that was 7.2 M in H_2SO_4 , 23% from a solution that was 10.8 M in H_2SO_4 , and 3% from a solution that was 14.4 M in H_2SO_4 . Throughout all the distillations the dichromate in the reaction mixture was not reduced with hydrazine; it was found that during the distillation the oxidation of acetic acid was negligible.

Since the sulfuric acid concentration of the reaction mixture in the first of the above three experiments approaches that employed by Ginger,² the stability of acetic acid was studied by using the quantity of acid employed by Kuhn and Roth and by Ginger. The results are shown at three temperatures in Figs. 5, 6, and 7. Figure 5 shows that at $150^\circ C$ the rate of oxidation of acetic acid is rapid when the sulfuric acid concentration in the reaction mixture is 3.6 M (1 ml of concentrated H_2SO_4) or 6.0 M (2 ml of concentrated H_2SO_4). When 6 M $NaHSO_4$ is used as the source of hydrogen ion, however, the rate of oxidation of acetic acid is reduced sufficiently so that it might be used in place of sulfuric acid if the oxidation of the organic compound to acetic acid in the bisulfate solution were sufficiently rapid.

Figure 6 shows the rate of oxidation of acetic acid at the temperature usually prescribed for sealed-tube digestions, $120^\circ C$, when the sulfuric acid concentration is 3.6 M or 6 M and when 6 M $NaHSO_4$ is used as the hydrogen ion source. The oxidation is sufficiently slow at this temperature that digestion periods as long as 8 hours do not produce serious loss of acetic acid. Figure 7 illustrates the rate of oxidation at $100^\circ C$ for the three reaction mixtures.

The three figures also show the rate of oxidation of benzoic acid in 4 N chromic acid and 3.6 M H_2SO_4 , at the three temperatures studied. The comparatively rapid oxidation of benzoic acid permits the determination of terminal methyl groups in the presence of benzoyl or benzoate groups, provided the digestion time is extended to a period considerably longer than usually recommended for the terminal methyl determination.

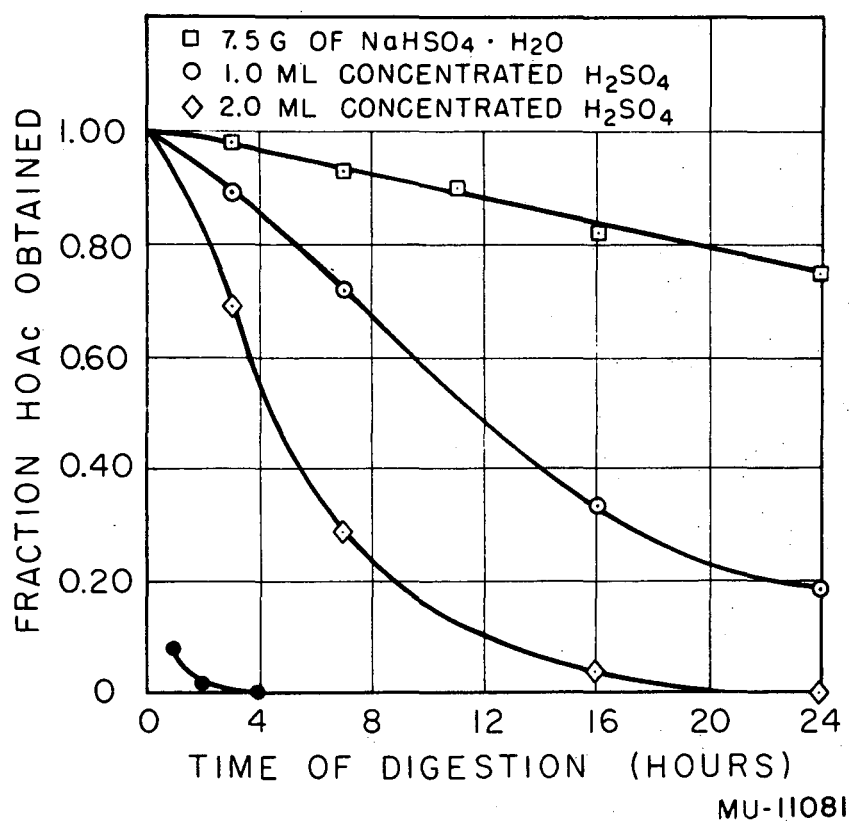
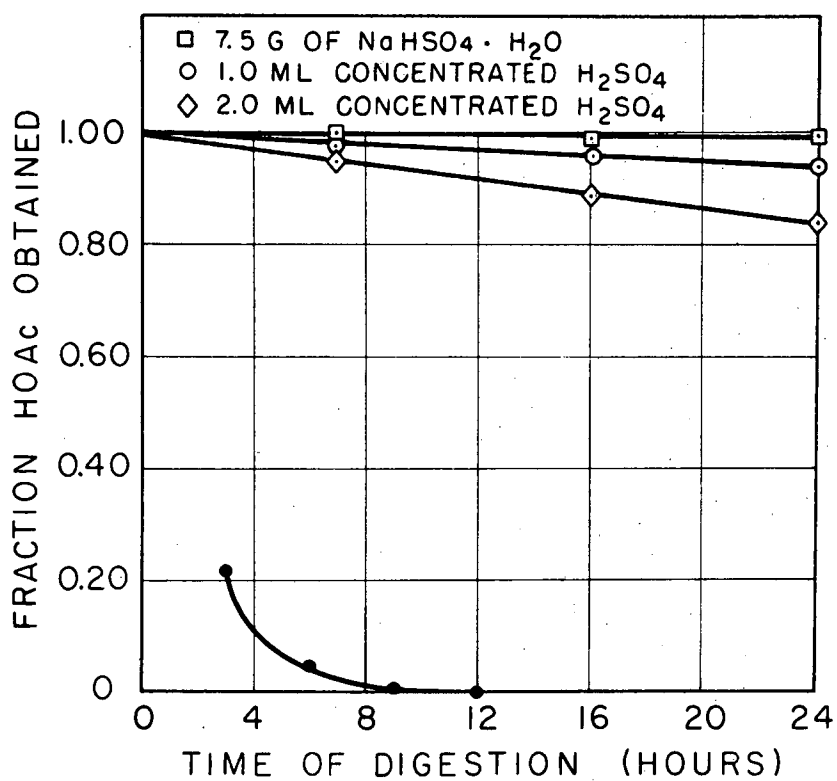
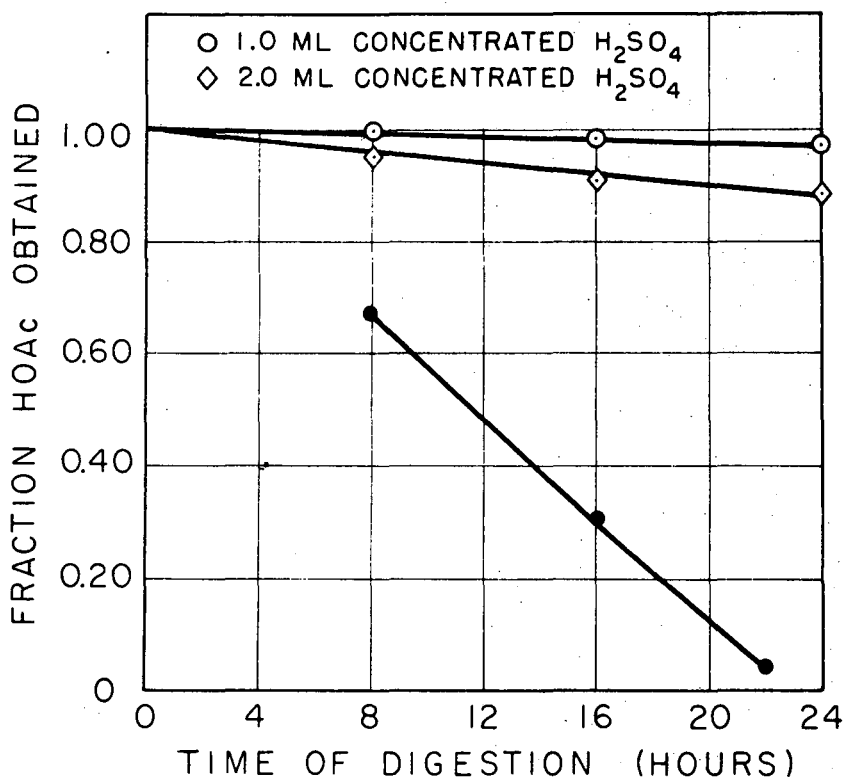


Fig. 5. The rate of decomposition of 0.06 mmole of acetic acid at 150°C in a reaction mixture which contains 4 ml of 5 N chromic acid plus (a) 1 ml of concentrated sulfuric acid, (b) 2 ml of concentrated sulfuric acid, and (c) 7.5 g of sodium hydrogen sulfate. The three solid circles represent the rate of decomposition of 0.06 mmole of benzoic acid in a reaction mixture containing 1.0 ml of concentrated H_2SO_4 and 4 ml of chromic acid.



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Fig. 6. The rate of decomposition of 0.06 mmole of acetic acid at 120°C in a reaction mixture which contains 4 ml of 5 N chromic acid plus (a) 1 ml of concentrated sulfuric acid, (b) 2 ml of concentrated sulfuric acid, and (c) 7.5 g of sodium hydrogen sulfate. The solid circles represent the rate of decomposition of 0.06 mmole of benzoic acid in a reaction mixture containing 1.0 ml of concentrated H₂SO₄ and 4 ml of 5 N chromic acid.



MU-11083

Fig. 7. The rate of decomposition of 0.06 mmole of acetic acid at 100°C in a reaction mixture which contains 4 ml of 5 N chromic acid plus (a) 1 ml of concentrated sulfuric acid, and (b) 2 ml of concentrated sulfuric acid. The solid circles represent the rate of decomposition of 0.06 mmole of benzoic acid in a reaction mixture containing 1.0 ml of concentrated H₂SO₄ and 4 ml of 5 N chromic acid.

The Determination of Terminal Methyl Groups in Some Simple Aliphatic Compounds

Campbell and Morton¹ concluded, on the basis of their work, that $(\text{CH}_3)_2-\text{C}$ and $(\text{CH}_3)_3-\text{C}$ -groups form acetic acid upon digestion with the chromic acid reaction mixture, and that acetone is not a stable product in the oxidation step. However, this leaves unexplained the loss of 15% to 25% of the expected amount of acetic acid in the relatively simple samples they analyzed. For comparison, this study includes determinations of a number of simple compounds, and their results are tabulated in Table I. In all of the analyses listed in this table, 4 ml of chromic acid and 1 ml of concentrated sulfuric acid were used as the oxidation mixture. The length of time of digestion is noted for each determination.

Table I

Acetic acid recovered from the oxidation of some simple aliphatic compounds. Reaction mixture contains 4 ml of 5 N chromic acid and 1 ml of concentrated sulfuric acid. Digestion temp. = 120°C.

Sample	Digestion time (hours)	<u>Moles HOAc per mole of compound</u>	
		Found	Present
acetone	1/4	0.98	1
	1/2	0.99	
	4	0.99	
mesityl oxide	1/2	1.95	2
	1	1.98	
	2	2.00	
isovaleric acid	1	0.96	1
	2	0.99	
	4	0.98	
t-amyl alcohol	1	1.92	2
	2	1.96	
	4	1.96	
trimethyl acetic acid	2	0.92	1
	4	0.96	
t-butyl alcohol	2	0.98	1
	4	0.99	

With the exception of trimethyl acetic acid, the Kuhn-Roth reaction mixture yields the theoretically expected amount of acetic acid for the simple compounds studied. Although the data are not listed, the reaction mixture containing 2 ml of concentrated sulfuric acid used by Ginger yields comparable results.

Low-molecular-weight amines do not yield acetic acid quantitatively when oxidized with the chromic acid reaction mixture. Table II lists the results of the digestion of several such compounds with the Kuhn-Roth reaction mixture at 120°C. The period of digestion is listed for each determination.

Table II

Acetic acid recovered from the oxidation of some simple aliphatic amines. Reaction mixture contains 4 ml of 5 N chromic acid and 1 ml of concentrated sulfuric acid. Digestion temp. = 120°C.

Sample	Digestion time (hours)	Moles HOAc per mole of <u>compound</u>	
		Found	Present
n-butyl amine	1/4	0.54	1
	1/2	0.66	
	1	0.73	
	2	0.72	
n-amyl amine	1	0.89	1
	2	0.89	
n-hexyl amine	1	0.69	1
	2	0.88	
triethyl amine	1	0.12	3
	2	0.06	
tri-n-butyl amine	4	2.22	3

The Determination of Terminal Methyl Groups in Several More Complex Aliphatic Compounds

The effects of varied digestion conditions on four compounds were studied: three of these were fatty acids--stearic acid, 18-n-propylheneicosanoic acid, and 2,3,4-trimethylhexadecanoic acid. The fourth was 5,5-dimethyl-1,3-cyclohexanedione. This compound was selected for study because it was thought that it might be a bridge to a better understanding of the oxidation of compounds containing a benzene ring. Figures 8 through 11 show the fractions of acetic acid obtained in the dichromate oxidation using the Kuhn-Roth digestion mixture and the increased amount of sulfuric acid recommended by Ginger at 120°C. The dashed lines in all four figures represent the rates of decomposition of acetic acid in the reaction mixture at the same temperature as shown in Fig. 6. It is interesting that all four compounds yield a greater quantity of acetic acid at the end of a 90-minute digestion period using Ginger's modification. Figure 8 shows that the time required to produce the maximum amount of acetic acid from stearic acid is increased fourfold by using the Kuhn-Roth procedure rather than the Ginger modification, but within experimental error the same total amount of acetic acid is obtained by either procedure. The oxidation of 18-n-propylheneicosanoic acid by the Kuhn-Roth procedure yields two moles of acetic acid per mole of sample very nearly quantitatively, as shown in Fig. 9. For this compound the greater amount of sulfuric acid employed in the Ginger modification apparently enhances the destruction of the terminal methyl groups at a rate sufficiently rapid to result in the formation of about 13% less acetic acid than was produced by the Kuhn-Roth reaction mixture. Figure 10 shows the results of the oxidation of 2,3,4-trimethylhexadecanoic acid by the two mixtures. Again the oxidation is more rapid when 2 ml of concentrated sulfuric acid is used, but a greater yield of acetic acid is obtained from the four terminal methyl groups when the smaller amount of acid is employed. The results of the analyses of these two samples suggest that still further reduction of the sulfuric acid concentration may yield acetic acid more nearly quantitatively if the required digestion period is not increased unreasonably. Figure 11 shows the very slow oxidation of 5,5-dimethyl-1,3-cyclohexanedione by either reaction mixture. After a digestion period of 24 hours the oxidation

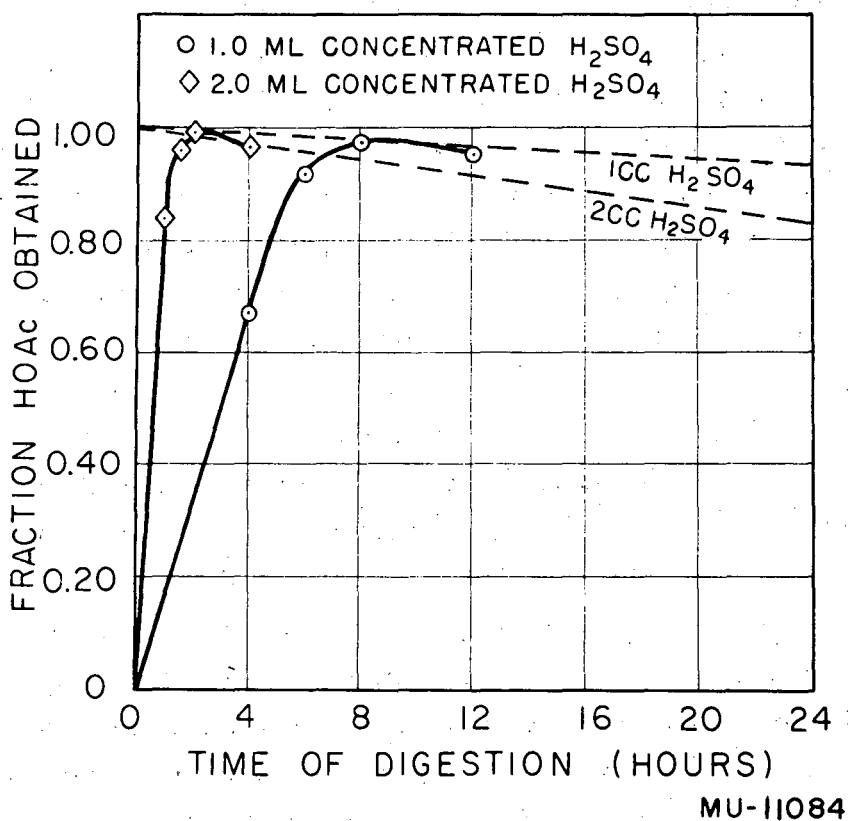


Fig. 8. The rate of formation of acetic acid from 0.06 mmole of stearic acid at 120°C in a reaction mixture which contains 4 ml of 5 N chromic acid and (a) 1 ml of concentrated sulfuric acid (b) 2 ml of concentrated sulfuric acid.

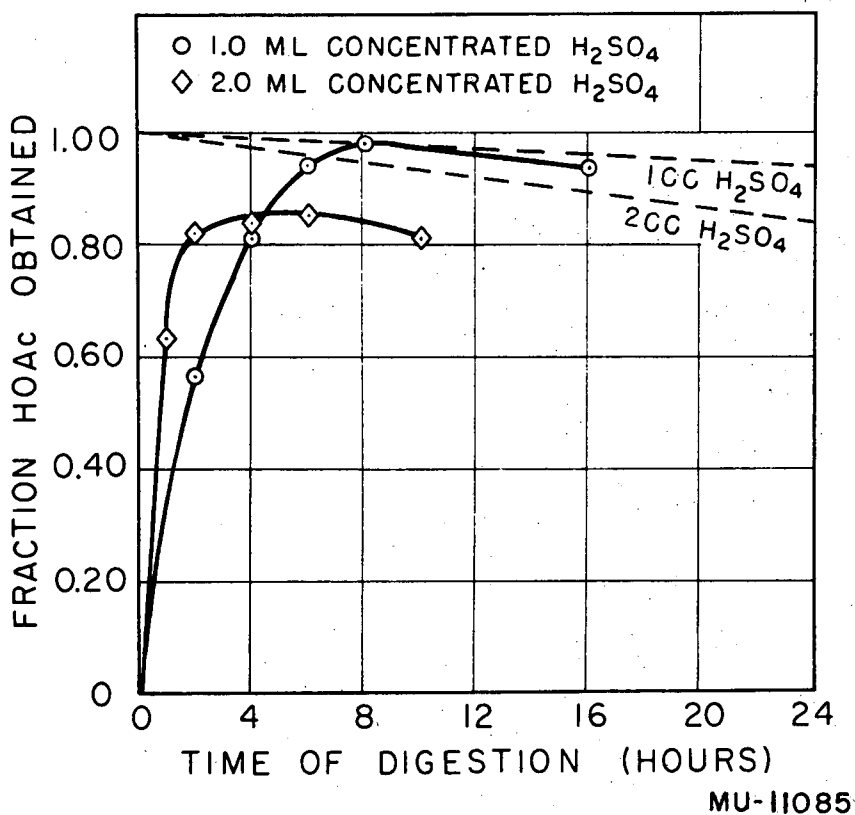


Fig. 9. The rate of formation of acetic acid from 0.03 mmole of 18-n-propylheneicosanoic acid at 120°C in a reaction mixture which contains 4 ml of 5 N chromic acid and (a) 1 ml of concentrated sulfuric acid, (b) 2 ml of concentrated sulfuric acid.

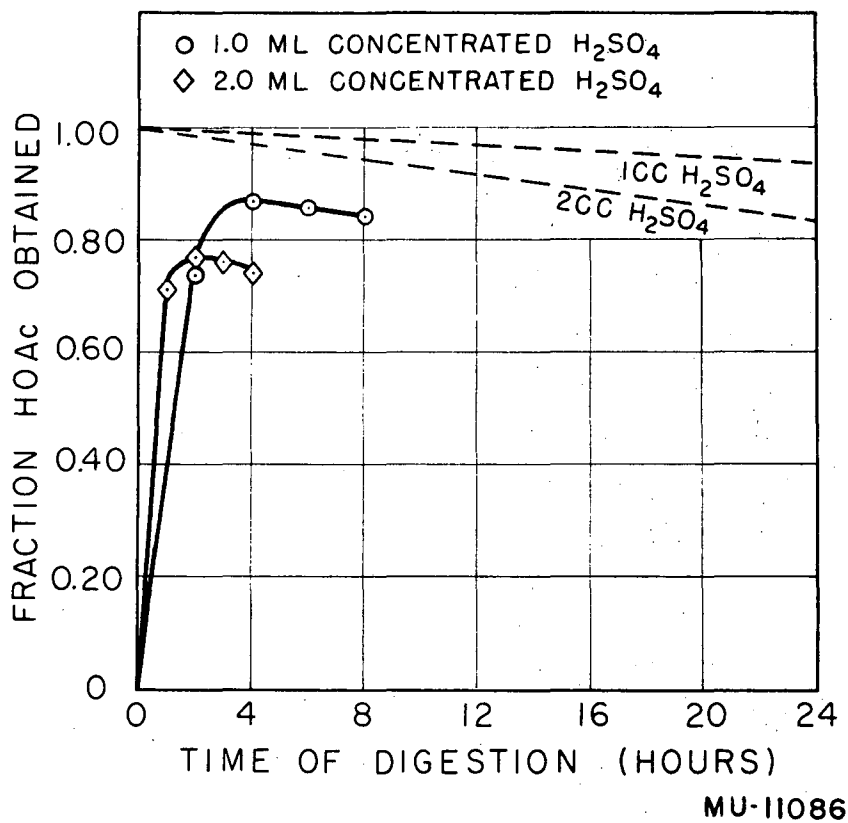
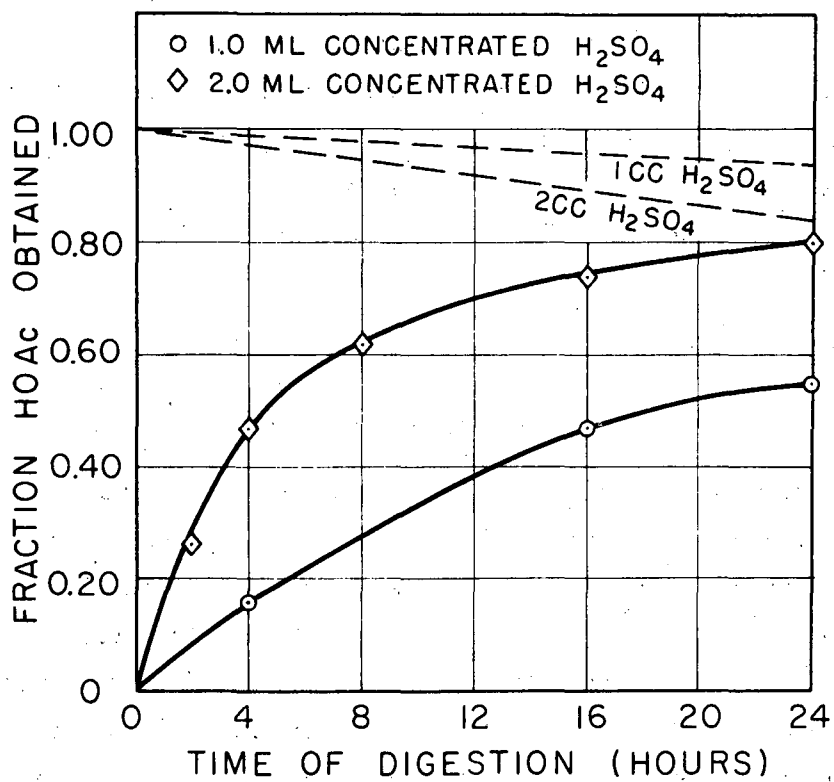


Fig. 10. The rate of formation of acetic acid from 0.015 mmole of 2, 3, 4-trimethylhexadecanoic acid at 120° C in a reaction mixture which contains 4 ml of 5 N chromic acid and (a) 1 ml of concentrated sulfuric acid, (b) 2 ml of concentrated sulfuric acid.

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MU-11087

Fig. 11. The rate of formation of acetic acid from 0.06 mmole of 5,5-dimethyl-1,3-cyclohexanedione at 120°C in a reaction mixture which contains 4 ml of 5 N chromic acid and (a) 1 ml of concentrated sulfuric acid, (b) 2 ml of concentrated sulfuric acid.

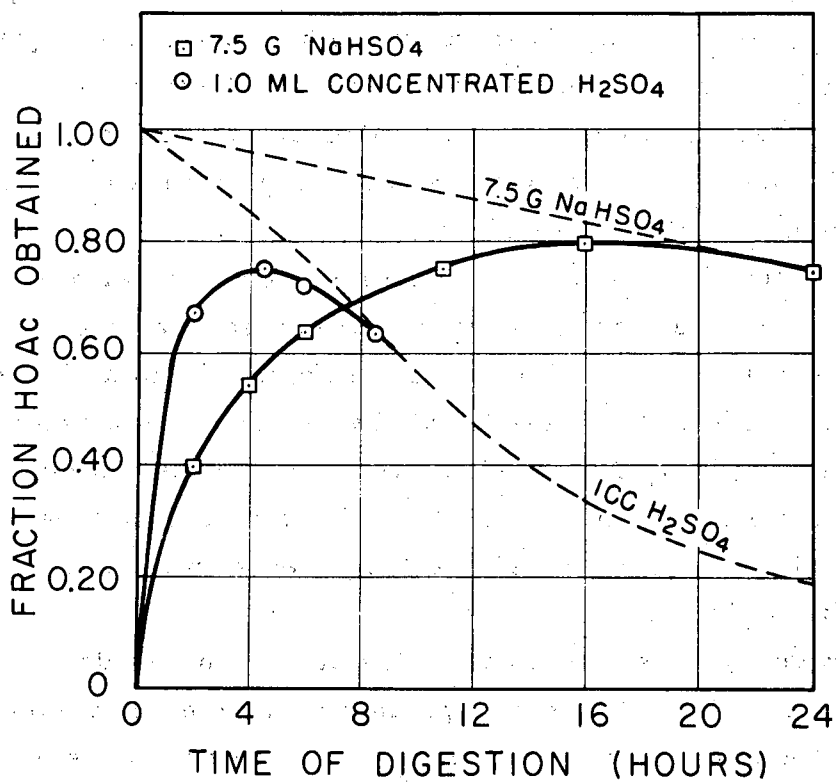
is nearly complete when the Ginger modification is used with the Kuhn-Roth oxidation mixture, digestion of the sample is not complete at the end of 24 hours, and the slow rate of formation of acetic acid illustrated in Fig. 11 indicates that considerably more time is required for complete digestion.

Because of the rapid destruction of acetic acid at 150°C few samples were digested at this temperature. The effect of increased temperature upon the digestion of 5,5-dimethyl-1,3-cyclohexanedione is interesting, however, because it does indicate that a temperature greater than 120°C may be desirable for the digestion of samples that are relatively stable to dichromate oxidation. Figure 12 shows the rate of formation of acetic acid with the Kuhn-Roth procedure, and also the milder oxidation mixture containing 7.5 g of sodium hydrogen sulfate. Both curves indicate that the gem-dimethyl group yields one acetic acid molecule, but that the relatively long time required for the oxidation destroys sufficient acetic acid so that the maximum amount produced approximates 75% to 80% of the total possible amount.

CONCLUSIONS

The present investigation is concerned only with the determination of terminal methyl groups attached to aliphatic compounds. A relatively limited number of substances have been studied, but the information permits a number of conclusions, and points the way to further study of the procedure. The study shows that the rate of distillation of acetic acid is speeded up appreciably by jacketing the distillation flask with toluene or n-butyl alcohol. Also it is seen that the oxidation of acetic acid at the temperature of distillation is so slow that there is no need to reduce the chromic acid with hydrazine or hydrogen peroxide.

At 150°C the Kuhn-Roth reaction mixture, and the one containing an increased amount of acid proposed by Ginger, oxidize acetic acid so rapidly that the results obtained are not satisfactory. At 120°C, the rate of oxidation of acetic acid is decreased-- a 20-hour digestion period is required to destroy 5% of the total acetic acid present by the Kuhn-Roth reaction mixture, whereas approximately 7 hours are required to destroy a like quantity if the Ginger reaction mixture is employed. No marked decrease



MU-11088

Fig. 12. The rate of formation of acetic acid from 0.06 mmole of 5,5-dimethyl-1,3-cyclohexanedione at 150°C in a reaction mixture which contains 4 ml of 5 N chromic acid and (a) 1 ml of concentrated sulfuric acid (b) 7.5 g of sodium hydrogen sulfate.

in oxidation occurs when the temperature is further lowered to 100°C at either acid concentration.

Acetic acid is considerably more stable to oxidation by chromic acid than is benzoic acid. Consequently, it is possible, by extension of the digestion period, to completely remove the benzoic acid while losing only a small amount of the acetic acid formed. Also it would be possible, by minimizing the digestion period and digestion temperature, to obtain an estimate of the sum of the two acids.

The chromic acid oxidation of t-butyl or t-amyl alcohol shows that one molecule of acetic acid is obtained quantitatively for the $(\text{CH}_3)_2-\overset{\curvearrowright}{\text{C}}$ or $(\text{CH}_3)_3-\text{C}-$ group present. These results plus the rapid and quantitative formation of acetic acid from acetone confirm the work of Campbell and Morton that acetone is not a stable product in the oxidation of these two groups. The determination of terminal methyl groups attached to aliphatic amines requires further study.

The results of the oxidation of the more complex aliphatic compounds reported in this investigation illustrate that a general procedure for the terminal methyl determination cannot be so rigidly established as that generally employed. The results in Figs. 9 and 10 show two instances wherein less acetic acid is obtained with the increased amount of sulfuric acid recommended by Ginger. Figure 11 indicates, however, that for 5,5-dimethyl-1,3-cyclohexanedione the greater sulfuric acid concentration is necessary at 120°C.

As a result of this investigation the authors have adopted a policy of determining terminal methyl groups under a single set of conditions only when it has been previously determined that the sample is easily digested or when the quantity of material available for analysis is the limiting factor. In general, the Kuhn-Roth reaction mixture is employed and the digestion periods for two samples of the substance to be analyzed are varied by a factor of two. These two results then serve as a basis for determining whether digestion is complete and, if necessary, what the conditions should be for further study.

In each terminal methyl determination the rate of destruction of acetic acid after digestion of the sample was slightly greater than that for the digestion of acetic acid itself. Westheimer⁴ states that +4 and +5 chromium

intermediates are produced during the reduction of dichromate and that at least one of these species is capable of oxidizing manganous ion to manganese dioxide. In the digestion of acetic acid as a control no appreciable reduction of dichromate occurs, while for a sample this is not true. It seems reasonable, therefore, that the presence of very small amounts of such a powerful oxidizing agent could be responsible for the slight difference in rate of oxidation of acetic acid in the two cases. Of course, one of these intermediates also could oxidize the terminal methyl group directly and thus be responsible for the low results shown in Figs. 9 and 10.

The design of the equipment used in this study is more elaborate than usually employed for the terminal methyl determination. However, the authors believe that the simplicity of operation, the reduced quantity of distillate required for quantitative recovery of acetic acid, and the complete elimination of sulfuric acid carry-over in the distillation step represent improvements to the method of analysis. In addition, the appreciably better results that have been obtained by using sealed tubes and the rocking furnace for the digestion of samples justify their use.

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