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AN INVESTIGATION OF THE MECHANISM OF THE DECOMPOSITION OF ACETYL PEROXIDE IN ACETIC ACID-2-C^{14} [1,2]

by

Arthur Fry[3], B. M. Tolbert, and Melvin Calvin

December 4, 1951

Berkeley, California

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ABSTRACT

1. The decomposition of diacetyl peroxide in acetic acid-2-C^{14} has been studied. The activity of the products in general confirmed the mechanism of the reaction as proposed by Kharasch and Gladstone.

2. The presence and distribution of activity in the methyl acetate produced in this reaction is not explained by the previously proposed mechanism.

3. There was no appreciable exchange of acetic acid and diacetyl peroxide under the conditions of the reaction.

4. Essentially no exchange of methyl acetate and acetic acid was observed when these reagents were heated at 100° for 5 hours.
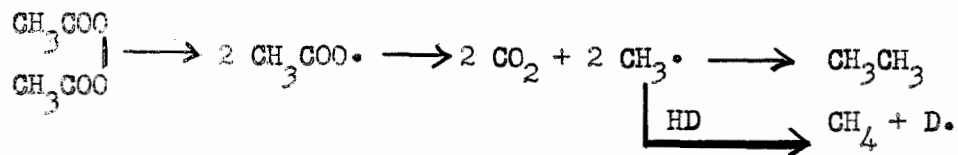
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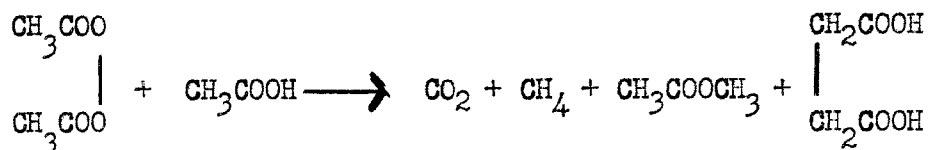
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The decomposition of acetyl peroxide in acetic acid solutions was first studied by Walker and Wild[4] who determined that the ratio of methane to ethane in the gas evolved increased with increasing concentration of acetic acid. The reaction was not carried out in glacial acetic acid, and no study was made of the non-gaseous products of the reaction. They suggested that the primary process was a dissociation of the peroxide into free acetate radicals which decomposed further to give carbon dioxide and free methyl radicals, which dimerized to give ethane or reacted with some hydrogen donor, HD, to give methane.

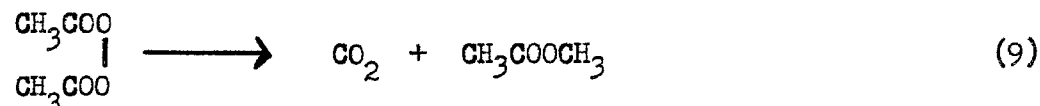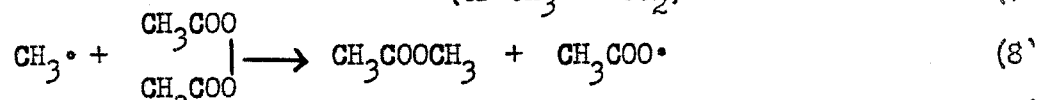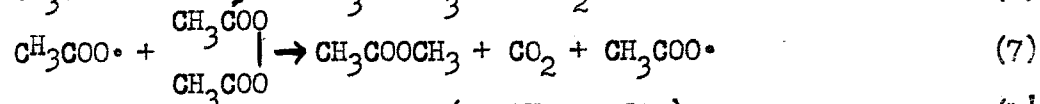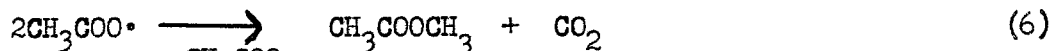$$\begin{matrix} CH_3COO \\ | \\ CH_3COO \end{matrix} \longrightarrow 2\ CH_3COO\cdot \longrightarrow 2\ CO_2 + 2\ CH_3\cdot \longrightarrow CH_3CH_3$$
$$\xrightarrow{\ HD\ } CH_4 + D\cdot$$

(4) O. J. Walker and G.L.E. Wild, J. Chem. Soc., 207 (1935); 1132 (1937).

Kharasch and Gladstone[5] studied the decomposition of acetyl peroxide in glacial acetic acid and in some of its derivatives, and found that succinic acid or its substitution derivatives were formed, along with carbon dioxide, methane, and some methyl acetate.

$$
\begin{array}{c}
CH_3COO \\
| \\
CH_3COO
\end{array}
+ CH_3COOH \longrightarrow CO_2 + CH_4 + CH_3COOCH_3 +
\begin{array}{c}
CH_2COOH \\
| \\
CH_2COOH
\end{array}
$$

No hydrogen or unsaturated gases were found although a careful search for these substances was made. No specific mention of ethane was made, although the hydrocarbon gas was stated to be 97-98% pure as shown by vapor pressure measurements at liquid nitrogen temperature and by molecular weight determinations. To explain the observed results, Kharasch and Gladstone proposed the following mechanism:[6]

$$
\begin{array}{c}
CH_3COO \\
| \\
CH_3COO
\end{array}
\longrightarrow CH_3 \cdot + CO_2 + \underset{(I)}{CH_3COO \cdot}
\tag{1}
$$

$$
CH_3COOH + CH_3 \cdot \longrightarrow Complex \longrightarrow CH_4 + \underset{(II)}{\cdot CH_2COOH}
\tag{2}
$$

$$
2 \cdot CH_2COOH \longrightarrow HOOCCH_2CH_2COOH
\tag{3}
$$

$$
CH_3COO \cdot \longrightarrow CH_3 \cdot + CO_2
\tag{4}
$$

$$
CH_3COO \cdot + HD \longrightarrow CH_3COOH + \cdot D
\tag{5}
$$

$$
2CH_3COO \cdot \longrightarrow CH_3COOCH_3 + CO_2
\tag{6}
$$

$$
CH_3COO \cdot +
\begin{array}{c}
CH_3COO \\
| \\
CH_3COO
\end{array}
\rightarrow CH_3COOCH_3 + CO_2 + CH_3COO \cdot
\tag{7}
$$

$$
(or \; CH_3 \cdot + CO_2)
\tag{7'}
$$

$$
CH_3 \cdot +
\begin{array}{c}
CH_3COO \\
| \\
CH_3COO
\end{array}
\longrightarrow CH_3COOCH_3 + CH_3COO \cdot
\tag{8'}
$$

$$
(or \; CH_3 \cdot + CO_2)
\tag{8'}
$$

$$
\begin{array}{c}
CH_3COO \\
| \\
CH_3COO
\end{array}
\longrightarrow CO_2 + CH_3COOCH_3
\tag{9}
$$
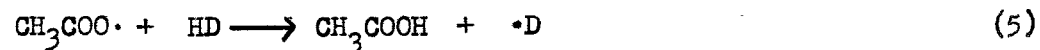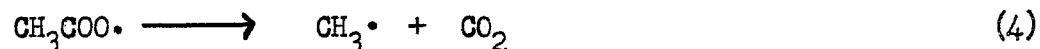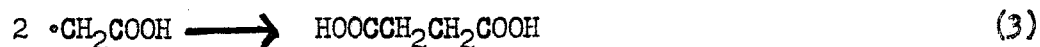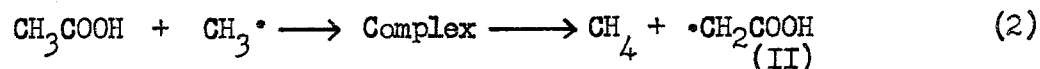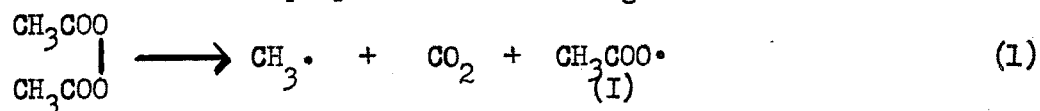
(5) M. S. Kharasch and M.T. Gladstone, J. Am. Chem. Soc., 65, 15 (1943)
(6) Some of these equations are written explicitly only in later papers by Kharasch

and co-workers, e.g., M. S. Kharasch, H. N. Friedlander and W. H. Urry, J. Org. Chem., 16, 533 (1951); M. S. Kharasch and G. Buchi, J. Am. Chem. Soc., 73, 632 (1951).
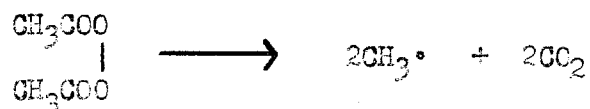
They were not able to account quantitatively for all the acetate radicals (I) formed in equation (1). The initial decomposition was considered to be by equation (1) rather than by direct decomposition to two methyl radicals and two molecules of carbon dioxide.

$$CH_3COO \atop | \atop CH_3COO \longrightarrow 2CH_3 \cdot + 2CO_2$$

They state: "The experience gained in this Laboratory by decomposing acetyl peroxide in many different solvents justifies the assumption that the peroxide when heated decomposes as follows:" (equation(1))

Most of the "experience" referred to unpublished work. In support of this assumption they point out that the yield of succinic acid is practically quantitative calculated on the basis of equations (1), (2), and (3). They apparently neglect the $CH_3 \cdot$ formed by equations (4), (7') and (8'), although the methane obtained (presumably only from $CH_3 \cdot$) amounts to 1.47 moles per mole of acetyl peroxide, and equations (1) and (2) would give only one mole.

They suggest that the free radical (II) would be stabilized by resonance.

$$\cdot CH_2 - \overset{O}{\underset{\|}{C}} - OH \longleftrightarrow CH_2 = \overset{O \cdot}{\underset{|}{C}} - OH$$

and thus would require a high energy of activation to react with the solvent, so its dimerization would be favored.

A check on the above mechanism has been carried out by decomposing acetyl peroxide in acetic acid-2-C^{14}. According to the above equations the distribution of radioactivity in the products would be as follows:

$$
\begin{matrix} CH_3COO \\ | \\ CH_3COO \end{matrix} + C^*H_3COOH \longrightarrow CO_2 + CH_4 + CH_3COCCH_3 + \begin{matrix} C^*H_2COOH \\ | \\ C^*H_2COOH \end{matrix}
$$
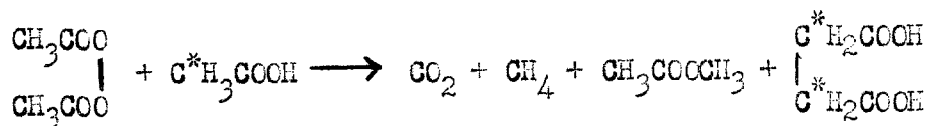
The methylene groups of the succinic acid would be labeled with the same specific activity as the methyl group of the acetic acid, while the other three products, carbon dioxide, methane, and methyl acetate would be completely inactive.

PROCEDURE AND RESULTS

Preliminary Study of the Exchange between Actyl Peroxide and Acetic Acid. - The possibility of exchange between acetyl peroxide and acetic acid had to be examined as as preliminary to the decomposition experiments. Solid, unlabeled acetyl peroxide was dissolved in acetic acid-2-C^{14} and the solution allowed to stand, first for one hour at room temperature, and latei for one week at room temperature followed by six hours at 53°C. The peroxide concentration of the solution remained constant throughout this experiment.

After standing, the solution was dissolved in water and extracted four times with equal volumes of carbon tetrachloride. The first carbon tetrachloride extract was back-extracted two additional times with equal volumes of water. Distribution ratio studies had shown that this extraction procedure was adequate for the quantitative separation of acetyl peroxide and acetic acid. The final aqueous and carbon tetrachloride solutions contained the purified acetic acid and acetyl peroxide, respectively.

The acetyl peroxide was reduced to acetic acid with iodide ion in sulfuric acid solution. This acetic acid was purified by steam distillation and the two samples of acetic acid were counted as sodium acetate.

The results of the exchange studies are given in Table I:

TABLE I

Acetyl Peroxide-Acetic Acid Exchange Studies

Exchange Conditions	Specific Activity, cts./min/mg. CH_3CCONa			
	Original		Recovered	
	Acetic Acid	Acetyl Peroxide	Acetic Acid	Acetyl Peroxide
1 hr. at ~23°C.	273 ± 8	0	258 ± 8	-1.7 ± 2
1 week at ~23°C. followed by 6 hrs. at 53°C.	288 ± 9	0	239 ± 7	0.85 ± 2

It is seen that within the experimental counting error, none of the activity in
the acetic acid was found in the acetyl peroxide. The fact that the recovered acetic
acid had a lower specific activity than the original acetic acid used is probably
due to some non-reversible hydrolysis of the acetyl peroxide during the separation
procedure.

It is true that these exchange studies were not carried out under the con-
ditions of the reaction, and that under these conditions exchange might still occur.
However, the specific activity of the methane obtained from the decomposition
serves as a very sensitive measure of the exchange under the actual reaction con-
ditions. This will be considered in detail later.

Decomposition of Acetyl Peroxide in Acetic Acid

Acetyl peroxide dissolved in acetic acid-2-C^{14} was decomposed by adding it
dropwise to acetic acid-2-C^{14} maintained at 85-95°C. according to the procedure
of Kharasch and Gladstone[5]. The apparatus is shown in Figure 1. The reaction
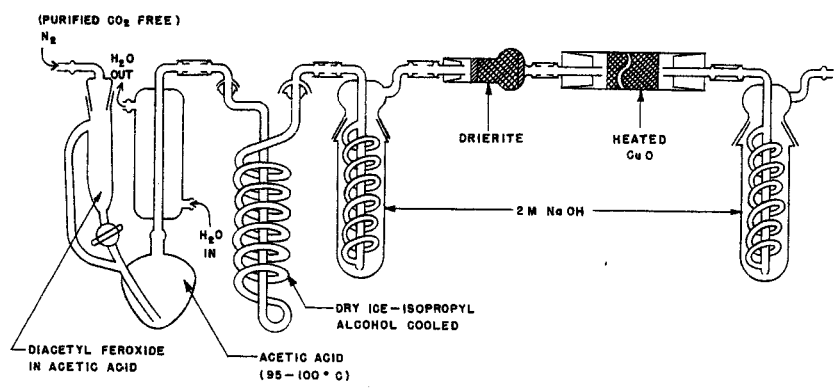
Fig. 1

vessel was swept with a slow stream of nitrogen which passed, in turn, through a water condenser, a spiral trap cooled by a dry ice-isoprophyl alcohol bath, a spiral bubbler filled with 2 $\underline{N}$ carbonate-free sodium hydroxide, a Drierite tube, a copper oxide packed furnace maintained at about 700°C. and a second sodium hydroxide filled bubbler. The water condenser returned most of the acetic acid to the reaction flask. The cold trap condensed out the methyl acetate and the remainder of the acetic acid. The carbon dioxide was collected in the first sodium hydroxide bubbler and the methane was burned in the furnace and the resulting carbon dioxide collected in the second sodium hydroxide bubbler.

In order to insure complete removal of the volatile reaction products, the gas sweep was continued for about one hour after bubbles were no longer observed in the reaction flask. At the end of this time, a sample of the solution in the reaction vessel always showed a negative test for oxidizing power when added to warm acidified iodide solution.

The acetic acid in the reaction flask was then steam distilled away from the succinic acid and recovered as sodium acetate. The succinic acid was obtained by a sixteen-hour continuous ether extraction, evaporation of the ether and re-crystallization of the residue from water.

The aqueous phase from the ether extraction always contained a small amount of acidic residue which was not identified further, but which was presumably a higher molecular weight polybasic acid, perhaps formed by dimerization of free radicals formed by the attack of methyl radicals on succinic acid or by their reacting with the free radical (II). Such an attack is indicated by the fact that lower rather than higher yields of succinic acid were obtained by increasing the ratio of acetyl peroxide to acetic acid during the decomposition as in runs 3, 4, and 7. This would be predicted from the work of Kharasch and co-workers who have shown that a tertiary hydrogen atom is more readily removed from a

molecule by a free radical than a secondary hydrogen, which, in turn, is more readily removed than a primary hydrogen.

Representative molar ratios of products obtained are shown in Table II where they are compared with the corresponding values obtained by Kharasch and Gladstone[5].

TABLE II

Molar Ratios of Products Obtained in the Decomposition
of Acetyl Peroxide in Acetic Acid

Moles X/Moles Acetyl Peroxide

Experiment \ X =	Beginning Acetic Acid	Carbon Dioxide	Methane	Succinic Acid
Kharasch and Gladstone[5]	34.7	1.53	1.43	0.50
This work[*]	37	1.54	1.13	0.40
(*) Data averaged from 8 runs				

The relative specific activities of the various reaction products are shown in Table III expressed as percentages of the specific activity of the methyl group of the acetic acid-2-C^{14} used. All of the products were burned to carbon dioxide and counted as barium carbonate. The treatment of the methyl acetate fractions will be treated in detail below.

Investigation of Distribution of Activity in Methyl Acetate Fraction

The methyl acetate obtained from the reaction, in agreement with the observation of Kharasch and Gladstone[5], was found as a liquid in the bottom of the spiral trap which had been cooled to ∿-80°C. A small amount of acetic acid was also found in this trap, usually condensed as a solid film near the inlet end of the spiral.

TABLE III

Relative Specific Activity(****) of Reactants and Products Expressed as Percentage of Specific Activity of Methyl Group of Acetic Acid

Run No.	Acetic Acid Used (*)	Acetyl Peroxide Used	CO_2 Produced	CH_4 Produced	Succinic Acid Produced	Acetic Acid Recovered (*)	Methyl Acetate Produced	
							Acetate Fragment(*)	Alcohol Fragment
1	100(**)	0	0.00 ± 0.1	0.07 ± 0.1	97.8 ± 2.0	101.5 ± 2.0	<28	
2	100	0	0.01 ± 0.1	0.16 ± 0.1	93.7 ± 2.0	103.0 ± 2.0	<28	
3(***)	100	0	0.06 ± 0.1	0.60 ± 0.1	--	100.0 ± 2.0	<28	
4(***)	100	0	0.00 ± 0.1	0.34 ± 0.1	--	99.6 ± 2.0	<9.5	
5	100	0	0.00 ± 0.1	1.64 ± 0.1	97.2 ± 2.0	99.8 ± 2.0	<12.3	
6	100	0	0.00 ± 0.1	2.50 ± 0.1	--	98.0 ± 2.0	32.5 ± 0.6	3.19 ± 0.1
7(***)	100	0	0.07 ± 0.1	0.36 ± 0.1	--	103.4 ± 2.0	13.5 ± 0.3	2.71 ± 0.1

(*) Methyl or methylene group only.

(**) Actual specific activity = 5.20 ± 0.11 x 10⁴, or 9.96 ± 0.20 x 10³ dis./min./mg. CH_3-carbon.

(***) Ratio of acetic acid to acetyl peroxide used = 8 instead of 37.

(****) The errors expressed in this table are probable counting errors. The actual errors may be somewhat larger.

On a preliminary run the liquid in the bottom of the spiral trap was poured out
and a micro boiling point determination was made. B.P. = 57-59°C; reported for
methyl acetate, 59-60°C.

The activity values for methyl acetate for runs 1-4 given in Table III
are upper limits. In these runs the entire contents of the cold trap were
swept through the furnace by an oxygen stream, and the resulting carbon dioxide
collected as barium carbonate. Since the trap was known to contain acetic
acid-2-C^{14}, the activity might all have come from this. At any rate, these
experiments showed that the methyl acetate at least had a considerably lower
specific activity than the acetic acid.

In run 5, in order to remove the acetic acid from the methyl acetate,
the contents of the cold trap were vaporized into a stream of nitrogen, which
was then passed in turn through a spiral bubbler filled with ethanolamine main-
tained at 90-95°C., a drying tube tightly tube tightly packed with glass wool
to remove any entrained ethanolamine, the copper oxide packed furnace and a
spiral bubbler filled with 2 N sodium hydroxide. The sodium hydroxide bubbler
was changed periodically and the carbon dioxide precipitated as barium carbonate.
The specific activity was 564/dis./min./mg.C., while the specific activity of
the barium carbonate from the acetic acid used was 4.56×10^3 dis./min./mg.C.
The reaction was continued until no more barium carbonate was obtained. The
total barium carbonate obtained weighed 0.329 g. The ethanolamine had pre-
viously been distilled and all low boiling material removed. A blank run
was conducted under the same conditions as above but with no methyl acetate
present, and only 0.003 g. of barium carbonate was obtained. These results
show that there is activity in that part of the methyl acetate fraction which
comes through an ethanolamine bubbler at 90° - 95°C., but does not prove that

the volatile material is methyl acetate, nor does it eliminate entirely the possibility that the activity is due to acetic acid not bound by the amine.

In order to see if methyl acetate would come through the above ethanolamine procedure unchanged, a sample of known methyl acetate, B.P. 57-60°C., was subjected to the above procedure, except that the volatile material coming through the amine bubbler was collected in a spiral trap cooled to $\sim$ -80° C. Approximately three cc. of material was collected, and on distillation had a distilling range of 53-60°C. In runs 6 and 7 a positive identification of the volatile material was made by hydrolysis to methyl alcohol and acetic acid, as described later.

To check the possibility that the activity in the volatile fraction from the ethanolamine procedure might be due to acetic acid not bound by the amine, a synthetic mixture approximating the contents of the cold trap was prepared from two drops of inactive methyl acetate and two drops of acetic acid-2-C^{14}. The mixture was allowed to stand overnight at room temperature and was then carried through the ethanolamine procedure as described above. The activity of the barium carbonate obtained was 18 dis./min./mg.C. while the activity of the starting acetic acid was 2.60×10^4 dis./min./mg.C. This quite conclusively indicates that little, if any, acetic acid comes through the etthanolamine and, therefore, from the results of run 5, that there definitely is activity in the methyl acetate produced in the reaction. Incidentally, the above experiment also sets an upper limit on the amount of exchange between acetic acid and methyl acetate under these conditions.

In order to test the possibility that the activity in the methyl acetate might be due to exchange between acetic acid-2-C^{14} and methyl acetate during the reaction, the above experiment was repeated under more drastic and more closely controlled conditions. Weighed quantities of methyl acetate and acetic acid-2-C^{14} were mixed and heated on a steam bath for five hours in a closed vessel. At the end of this time, the mixture was vaporized into a nitrogen stream and carried through the ethanolamine procedure as before. The activity of the barium carbonate obtained was 19.7 dis./min./mg.C., while the activity of the acetic acid-2-C^{14} used was 2.60×10^4 dis./min./mg.C. Assuming that the material which came through the ethanolamine was pure methyl acetate, the activity value of 19.7 dis./min./mg.C. is 0.33% of the value calculated for complete exchange. The barium carbonate obtained only amounted to 56.3% of the theoretical amount for complete combustion of the methyl acetate, and we might assume that part of the methyl acetate was hydrolyzed by the ethanolamine. Making this assumption and assuming that all the methyl alcohol from the hydrolysis came through while only enough methyl acetate came through to account for the amount of barium carbonate obtained, we can calculate that the value of 19.7 dis./min./mg.C. is 0.45% of the value calculated for complete exchange. This value is then an upper limit for the amount of exchange, and the actual value is somewhere between this value and the 0.33% figure. We can therefore conclude that very little, if any, of the activity in the methyl acetate is due to exchange with acetic acid-2-C^{14} during the decomposition.

Having thus established the presence of activity in the methyl acetate, it was still necessary to study its distribution between the

two methyl groups of the molecule. The methyl acetate from runs 6 and 7 was
degraded as described below.

In run 6, the methyl acetate was carried through the ethanolamine
procedure and collected in a trap cooled to -80°C. The trap contents
were then distilled on a vacuum line into a vessel containing excess
sodium hydroxide solution, which was then closed off and heated on the
steam bath for two hours. Previous work on inactive methyl acetate
samples had shown that this procedure resulted in quantitative hydrolysis
of the ester. The vessel was again connected to the vacuum line, and the
methyl alcohol and water were distilled back into a spiral trap, leaving
a residue of dry sodium acetate and excess sodium hydroxide. The methyl
alcohol-water mixture was vaporized into a nitrogen stream and passed
through the furnace. The resulting carbon dioxide was collected as barium
carbonate. Its activity is given in Table III. The sodium acetate-sodium
hydroxide mixture was acidified and steam distilled. The activity of
the resulting acetic acid is given in Table III. The yield of barium
carbonate from the methyl alcohol was 0.912 millimoles, while the yield
of acetic acid was 0.443 millimoles, thus indicating that a fairly large
fraction of the material coming through the ethanolamine was not methyl
acetate, but probably methyl alcohol.

In an effort to improve the separation of methyl acetate and acetic
acid so as to avoid the hydrolysis obtained with the ethanolamine procedure,
attempts were made to wash the mixture with sodium hydroxide, sodium car-
bonate, and sodium bicarbonate solutions. Since the methyl acetate avail-
able from one run amounted to only one or two drops, all the separation
and hydrolysis procedures were carried out on a vacuum line. The hydrolysis

of the ester during washing with sodium hydroxide and sodium carbonate solutions was found to be too rapid for practical separation, but with a sodium bicarbonate solution little hydrolysis was noted, and the separation was found to be satisfactory.

Accordingly, the methyl acetate from run 7 was washed with sodium bicarbonate solution and then hydrolyzed as described above for the ester from run 6. The yield of barium carbonate from the methyl alcohol was 3.50 millimoles and the yield of acetic acid was 3.60 millimoles, indicating that the separation procedure was satisfactory. The activities of the alcohol and acid are given in Table III.

DISCUSSION

From the data in Table III it can be concluded that within our experimental error the methylene groups of the succinic acid are labeled with the same specific activity as the methyl groups of the acetic acid used, and that the carbon dioxide is completely inactive. These results are in complete agreement with the mechanism proposed by Kharasch and Gladstone[5]. It should be pointed out that Kharasch and Gladstone's work on substituted acetic acids leads to the same conclusion in respect to the succinic acid. For instance, tetramethylsuccinic acid was obtained when acetyl peroxide was decomposed in isobutyric acid:

$$\begin{array}{c} CH_3COO \\ | \\ CH_3COO \end{array} + (CH_3)_2CHCOOH \longrightarrow \begin{array}{c} (CH_3)_2CCOOH \\ | \\ (CH_3)_2CCOOH \end{array}$$
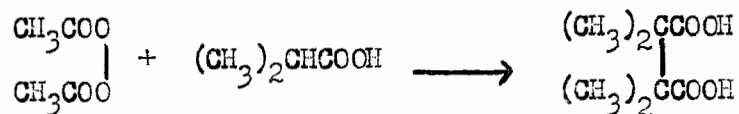
However, the presence of appreciable amounts of activity in the
methane and methyl acetate is not predicted by the mechanism of Kharasch
and Gladstone without modification. The considerable variability in the
specific activity of the methane would seem to indicate that some experi-
mental condition, perhaps temperature or rate of peroxide addition, is
not being adequately reproduced in the various runs. The difference in
the activity values between the various runs is at least partially ex-
plained in some cases by the different ratios of acetic acid to acetyl
peroxide used as indicated in Table III.

The Exchange between Acetyl Peroxide and Acetic Acid

As shown in Table I, there is no appreciable exchange between acetyl peroxide
and acetic acid at temperatures up to $\sim$ 50°C. This does not necessarily
mean that exchange cannot occur at 85-95°C., the conditions under which the
decomposition is carried out. However, an upper limit for the amount of
exchange under these conditions can very easily be established. The methane
evolved must certainly come from the methyl group of either the acetyl peroxide
or the acetic acid. Therefore, if we compare the specific activity of the
methane with the specific activity of all the methyl groups in the solution,
assuming complete exchange between the acetyl peroxide and acetic acid, we
have an upper limit for the amount of exchange. These calculated upper
limits are shown in Table V.

TABLE V

Upper Limits for the Exchange between
Acetyl Peroxide and Acetic Acid at 85-95° C.

Run	1	2	3	4	5	6	7
Exchange upper limit (%)	0.07	0.17	0.75	0.42	1.74	2.64	0.45

It is seen that even in the highest case the upper limit for the exchange

is 2.64%, and in most runs is considerably lower. It will be seen below

that there is an alternate and probably much more likely path for activity

to get into the methane, so the actual amount of exchange between acetic

acid and acetyl peroxide as such is probably very close to zero.

The Source of the Activity in the Methyl Acetate

According to the mechanism proposed by Kharasch and co-workers, equations

(1) - (9), none of the activity originally present in the acetic acid

would be found in the methane or methyl acetate. An obvious extension

of the above mechanism is the exchange between the acetate radicals and

acetic acid.

$$CH_3CCO\cdot + \overset{*}{C}H_3COOH \xrightleftharpoons{} CH_3COOH + \overset{*}{C}H_3COO\cdot \qquad (10)$$
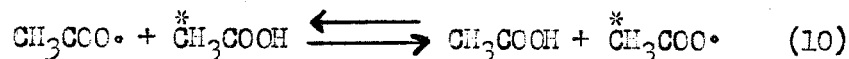
Such an exchange seems very likely and is considered by Waters[7] to be

(7) W. A. Waters, "The Chemistry of Free Radicals," Second Edition,

Oxford University Press, London, England (1948), p. 139.

an explanation of the relatively long life of the acetate radical. Such

an exchange is also indicated by the fact that Kharasch and Gladstone[5]

obtained methyl chloroacetate from the decomposition of acetyl peroxide in chloroacetic acid. This fact would also tend to support equation (7) as the most likely source of the methyl acetate.

Waters[8] also proposes another mode of formation of methyl acetate,

(8) Reference (7), pages 133-140.

equation (11).

$$CH_3COO\cdot + CH_3\cdot \longrightarrow CH_3COOCH_3 \qquad (11)$$

This coupled with equation (10) above could also explain the observed facts in the chloroacetic acid case. Kharasch and co-workers, however, do not consider this to be a very likely reaction path since both the methyl and acetate radicals must be present in small concentration.

If we consider again the equations for the formation of methyl acetate, (4), (6), (7), (8), (9),and (11), we see that all except (9) would give activity in the methyl acetate if the acetate radical were active. The exchange shown in equation (10) would accomplish this in a very reasonable manner. Equation (9) would still result in inactive methyl acetate, and hence cannot be the exclusive path of its formation. Also, the methyl chloroacetate could not have been formed by this path in the chloroacetic acid case.

If we consider equation (6) as the source of the methyl acetate, we see that the same specific activity would be found in both methyl groups since both come from the same source. From Table III we see that the two methyl groups are not equally labeled, and therefore equation (6) cannot be the exclusive path of formation of methyl acetate. Here again, the formation of methyl chloroacetate in the chloroacetic

acid case leads to the same conclusion.

If we consider equation (11), we see that the alcohol methyl group is formed from the methyl radical, and so is the methane, so both should have the same specific activity. Again from Table III we see that this is not true, and therefore equation (11) cannot be the exclusive path of formation of methyl acetate.

If we consider equations (7) and (8), we see that if either of these is the path of formation of methyl acetate, the three methyl groups necessarily must not become equivalent in the transition state, since this would again require equal specific activities in the two methyl groups of the methyl acetate. Further, since the alcohol methyl group has the lower specific activity, it must come chiefly from the acetyl peroxide, while the acid methyl group must come chiefly from the acetate radical and the methyl radical in equations (7) and (8), respectively. In order to accomplish this, a very decided scrambling of atoms would be necessary in equation (8), and as a result this path of formation seems very unlikely. Also, here the specific activity of the acid methyl group and of the methane should be the same since they both come from the methyl radical, but it is readily seen from Table III that this is not true. The chloroacetic acid case is also inconsistent with equation (8).

The presence of activity in the methane is readily explained by equation (4) assuming the acetate radical to be active (as by equation (10)). However, the amount of activity found in the methane also places an upper limit on the amount of acetate radical which can decompose by equation (4). Assuming that the specific activity of the acid methyl group of the methyl acetate is a reasonable lower limit[9] for the specific

(9) This is a very reasonable assumption since the acid methyl group
in the methyl acetate must arise directly from the acetate radical in
equations (6), (7), and (11), and any methyl acetate produced by equations
(8) or (9) would be inactive or nearly so, thus requiring a higher specific
activity in that methyl acetate produced from the acetate radical directly.

activity of the acetate radical, we can see that that portion of the

methane which arises from the methyl radical produced by equation (4)

will have the same specific activity as the methyl group of the acetate

radical. If we consider the case where the methane has the highest

specific activity, run 6, and set up an activity balance[10] for the methane,

(10) Activity in methane = total millimoles methane X specific activity
of methane = millimoles methane from equation (D) X specific activity of
methane from equation (D). Therefore:

$$\frac{\text{Millimoles methane from eq. (D)}}{\text{Total millimoles methane}} = \frac{2.50}{32.5} = 7.7\%$$

we see that at most 7.7% of the total methane could have come from the

acetate radical by equation (4). The corresponding figure for run 7 is

2.7%.

Having eliminated all the other paths of formation of methyl acetate

above, it would seem that equation (7) or (7') must be the major source

of the methyl acetate. If we assume that the primary decomposition of

the acetyl peroxide goes by equation (1), we can conclude from the above

paragraph and Table II that equation (7) cannot account for the experimental

results. If equation (7) were the path of formation of methyl acetate, the

only sources of methyl radical would be equations (1) and (4). In the

paragraph above we have shown that no more than 7.7% of the methane could

have arisen by equation (4). Equation (1) gives at most one mole of methane

even if the methyl radicals are removed by no other path. This makes

the total possible number of moles of methane per mole of acetyl peroxide

equal to 1.083. But as seen from Table II, more methane that this is always

produced, so we are left only with equation (7') as the major source of the

methyl acetate.

Now, if we examine equations (7'), (1), and (4), we can see that here

again we are limited to only one mole of methane per mole of acetyl

peroxide except for that formed by equation (4), since a given mole of

acetyl peroxide can decompose by equation (1) or (7'), but not by both.

By examination of all the equations, (1)—(11), it is seen that there is no

other case or combination of cases more favorable for the production of

methane. Therefore, if the calculation for the limitation of the amount

of acetate radical which can decompose by equation (4) is valid (and

we believe that it is), none of the above equations (and no combination

of them) will account for the experimentally observed results.

It might be observed that the ratio of methane to acetyl peroxide

obtained in this work is somewhat lower than that obtained by Kharasch

and Gladstone (Table II). No adequate explanation of this discrepancy

is known. It is possible that equation (4) has a large temperature

dependence, and that Kharasch and Gladstone's experiments were carried

out at a somewhat higher temperature than those in this work. Another

possible explanation is that our combusion procedure was not adequate

to burn the methane to carbon dioxide completely. Regardless of this

discrepancy, the above arguments still hold. If the second explanation

is correct, the actual values of the methane to acetyl peroxide ratio

in our work would be larger than those recorded in Table II, and the

above equations would then be even less adequate to explain the observed

results.

In order to explain the observed results, as shown above, it is necessary to find a source of methane instead of, or in addition to, the above equations. If we make the reasonable assumption that methane arises only from the methyl radical, it would seem that the original acetyl peroxide is the only likely source of free methyl radicals, and that the initial decomposition of acetyl peroxide is therefore not according to equation (1), but rather according to equation (12), where n is some fraction less than one.

The initial decomposition is actually probably a rupture into two acetate radicals since it is considered highly unlikely that two or more bonds in a molecule would be broken simultaneously. However, if this is the course of the reaction (or if the initial decomposition is by equation (1)), it must also be assumed that a fraction of the acetate radicals formed decompose very rapidly to carbon dioxide and methyl radicals before leaving the immediate area or decomposition, since after leaving this area these acetate radicals become indistinguishable from those which are undergoing equilibration by equation (10)[11].

(11) This assumes that we are dealing with an essentially steady state system.

This requires that the acetate radicals which undergo further rapid decomposition be different from those which are equilibrated by equation (10) since it has already been shown that the decomposition of acetate radicals by equation (4) is relatively slow after the exchange reaction (10). This is not unreasonable since part of the acetate radicals initially formed may well be in an unstable activated state which leads to further immediate decomposition, while the rest may be in a more stable state, perhaps with

the other fragments, carbon dioxide and methyl radicals, carrying off
the extra energy.

Regardless of the exact mechanics of this initial decomposition, a
short time after the initial break equation (12) adequately represents
the overall picture.

As previously mentioned the published justification for assuming
the initial decomposition to be by equation (1) does not seem too good.
However, these experiments also quite conclusively demonstrate that
acetate radicals are produced and that the initial decomposition is not
into two methyl radicals and two molecules of carbon dioxide, since in
this case no activity should be found in the methyl acetate.

By modifying the mechanism as proposed by Kharasch and co-workers
to assume that the initial decomposition is by equation (12), we see that
we can easily explain the experimentally observed facts. The same objec-
tions as before apply to equations (6), (8), (9), and (11), but it is
possible that the methyl acetate could be formed by the proper combina-
tion of equations (6), (9), and (11).

The preferred mechanism for the formation of the methyl acetate is
by equation (7) or (7'), with perhaps smaller amounts being formed in
the other possible ways. The proposed overall mechanism is shown diagrama-
tically in Chart I.

In view of the irreproducibility of the experimental values, some
question might be raised as to the validity of the conclusions drawn. How-
ever, limiting conditions have been used throughout the discussion, and
it is believed that no unjustified conclusions have been drawn.

The only real point of disagreement between this work and that of
Kharasch and Gladstone is in the formulation of the initial decomposition,

CHART I

The Mechanism of the Decomposition of Acetyl Peroxide in

Acetic Acid

$$CH_3COO$$
$$|$$
$$CH_3COO \longrightarrow (1+n)CH_3\cdot \;+\; \overset{a}{CH_3COOH} \longrightarrow \overset{c}{CH_4} + \overset{a}{\cdot CH_2COOH} \longrightarrow \overset{a\;\;a}{HOOCCH_2CH_2COOH}$$

$$+$$

$$\overset{b}{CH_3COO\cdot} \qquad\qquad (1+n)CO_2$$

$$\downarrow$$

$$CO_2 \qquad\qquad +$$

$$+ \qquad\qquad (1-n)CH_3COO\cdot \;+\; \overset{a}{CH_3COOH} \rightleftharpoons CH_3COOH \;+\; \overset{a}{CH_3COO\cdot}$$

$$\overset{b}{CH_3COOCH_3} \quad \overset{b}{CH_3\cdot} + CO_2 \longleftarrow \qquad\qquad b \qquad\qquad (*)$$

$$+$$

$$\overset{b}{CH_3COOCH_3}(**)(some)$$

$$+$$

$$CH_3COO\cdot$$
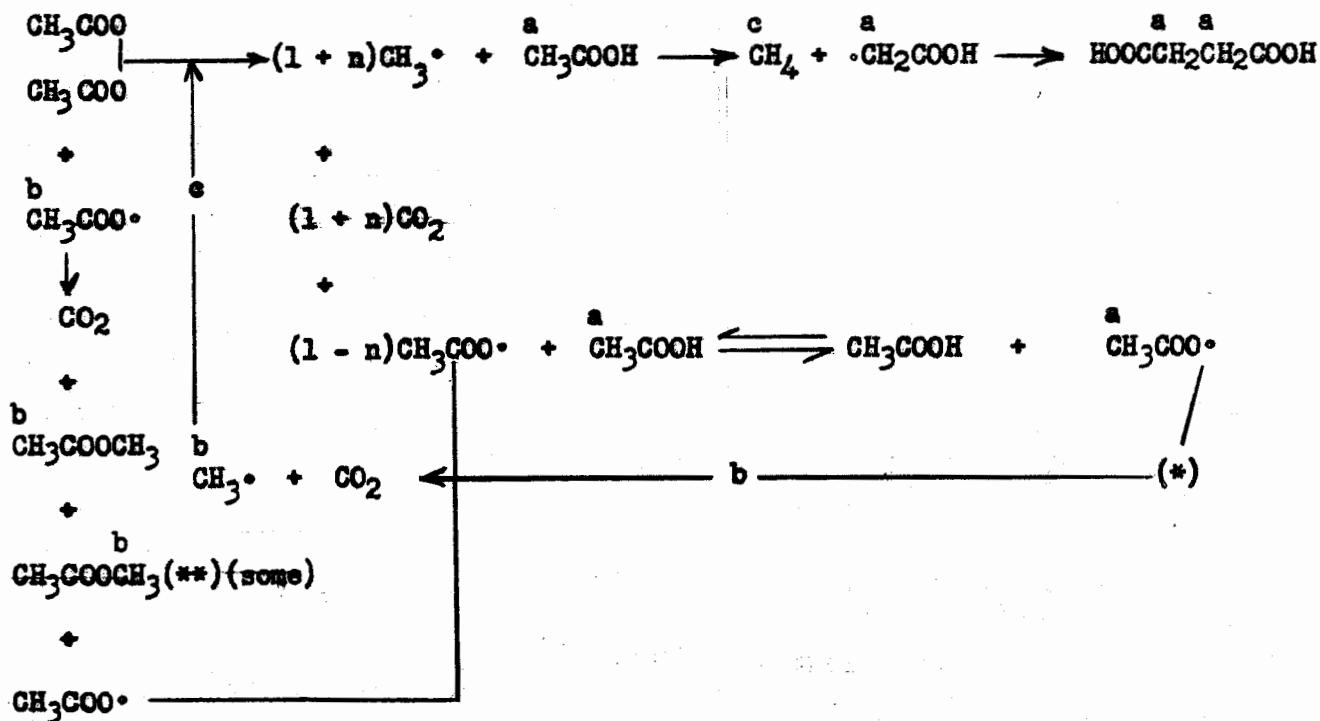
(*)   The solid lines connect various sources of the same species.

(**)   The activity in the alcohol methyl group of the methyl acetate may come from part of the methyl acetate being formed according to the equation

$$2\overset{b}{CH_3COO\cdot} \longrightarrow \overset{b}{CH_3COO}\overset{b}{CH_3} + CO_2$$

a,b,c   The superscripts denote specific activities. The small letters on the solid lines show the steady state specific activities of the methyl group in the species, averaged over all sources.

and as pointed out above the exact mechanics of this decomposition cannot
be regarded as settled. This work also serves to point out the improba-
bility of several of the possible paths for the formation of the methyl
acetate.

EXPERIMENTAL

Preparation of Acetic Acid-2-C^{14}

A one liter sample of glacial acetic acid was allowed to stand with
frequent shaking in a refrigerator for several hours. At the end of
this time about two-thirds of the acid had solidified. The liquid acid
was decanted and the residue allowed to stand at room temperature for a
few minutes with occasional shaking. The liquid acid was again decanted,
and the solid residue was melted and distilled at atmospheric pressure.
The first and last quarters of the distillate were discarded and the
middle half, B.P. = 118°C., was saved. Fifty grams of this acid were
allowed to stand for 72 hours at room temperature with 0.038 g. (20 μc)
of sodium acetate-2-C^{14} to effect complete exchange. The acetic acid-2-C^{14}
was then distilled away from the sodium acetate. The sodium acetate-2-C^{14}
was prepared by carbonation of the Grignard reagent prepared from methyl
iodide-C^{14} [12]

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(12) B. M. Tolbert, J. Biol. Chem., _173_, 205 (1948).

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Preparation and Analysis of Acetyl Peroxide

Acetyl peroxide was prepared according to the method of Gamborian[13] as modified by Kharasch, McBay, and Urry.[14]   Twenty grams of acetic anhydride,

(13) S. Gamborjan, Ber., 42, 4010 (1909).

(14) M. S. Kharasch, H. McBay, and W. H. Urry, J. Org. Chem., 10, 394 (1945)

10.0 g. of sodium peroxide and 100 cc. of diethyl ether were mixed together in an Erlenmeyer flask and cooled to -15°C. Thirty-five grams of crushed ice were gradually added over a 10-minute period with vigorous shaking. The ether solution was separated, dried with calcium chloride, and allowed to stand several hours in a dry ice-isopropyl alcohol bath. The acetyl peroxide crystallized out in beautiful long white needles, and the ether supernatant was drawn off with a filter stick. More dry ether was added, and the crystallization was repeated to insure removal of all the acetic anhydride and acetic acid. The last traces of ether were removed by evacuating to one mm. pressure for two hours.

All operations on the dry acetyl peroxide were carried out with tongs behind a safety shield, and the dry peroxide was dissolved in the solvent in which it was to be used as soon as possible to minimize the explosive possibilities.[15]   Throughout the preparation, yield was sacrificed to

(15) L. P. Kuhn, Chem. Eng. News, 26, 3197 (1948); E. S. Shanley, ibid., 27, 175 (1949).

safety, convenience, and purity. The weight of dry acetyl peroxide obtained in a representative run was 6.660 g. (44.1% based on sodium peroxide). The peroxide solutions were analyzed by the method of

Kokatnur and Jelling.[16]   The peroxide sample was dissolved in 99% isopropyl

alcohol, and one cc. each of glacial acetic acid and saturated potassium

(16) V. R. Kokatnur and M. Jelling, J. Am. Chem. Soc., 63, 1432 (1941).

iodide solution was added. The solution was heated almost to boiling and

maintained at that temperature for about five minutes. The solution was

then titrated without cooling with standard sodium thiosulfate. The oxygen

blank is negligible with this procedure. As a check on the purity of the

dry acetyl peroxide prepared as above, 0.2108 g. of solid acetyl peroxide

required 35.18 cc. of 0.1000 N sodium thiosulfate, corresponding to a weight

of 0.2095 g. Calc. purity = 99.4%.

Exchange of Acetic Acid-2-C^{14} with Acetyl Peroxide

The distribution ratios between CCl_4 and water were determined for acetyl

peroxide and acetic acid. Approximately 0.2 g. of solid acetyl peroxide

was dissolved in 10 cc. of carbon tetrachloride and extracted with 10 cc.

of water. The two phases were analyzed for peroxide as above. The carbon

tetrachloride phase required 2.40 cc. and the water phase required 0.68 cc.

of 0.1000 N sodium thiosulfate, giving a distribution ratio, $CCl_4/H_2O = 3.5$.

The experiment was repeated using 1 cc. acetic acid. The carbon tetra-

chloride phase required 0.42 and the water phase required 15.75 cc. of 1.000

N sodium hydroxide, giving a distribution ratio, $CCl_4/H_2O = 2.7 \times 10^{-2}$.

To study the exchange reaction a solution of 2.428 g. of solid acetyl

peroxide in 3.035 g. of acetic acid-2-C^{14} was prepared. The solution was

allowed to stand, first for one hour at room temperature and later for one

week at room temperature followed by 6 hours at 53°C. After standing, two cc.

portions of the solution were dissolved in water and extracted four times
with equal volumes of carbon tetrachloride. The first carbon tetrachloride
extract was back-extracted two additional times with equal volumes of
water. Using the above determined distribution ratios the final carbon
tetrachloride extract was calculated to contain 48% of the original acetyl
peroxide while the acetic acid-2-C^{14} should be reduced to 2.0×10^{-3} %
of its original value. The final aqueous phase was calculated to con-
tain 92% of the original acetic acid-2-C^{14} and 0.2% of the original
acetyl peroxide. The CCl_4 solution of acetyl peroxide was heated with
a dilute acidified solution of potassium iodide to reduce the peroxide to
acetic acid. The iodine formed was reduced to iodide ion with magnesium
metal, and the iodide ion was precipitated by adding silver sulfate. The
acetic acid was then steam distilled, titrated with sodium hydroxide, and
evaporated to dryness. The acetate samples were counted as sodium acetate
with the results given in Table I.

Decomposition of Acetyl Peroxide in Acetic Acid

Acetyl peroxide dissolved in acetic acid-2-C^{14} was decomposed by adding
it dropwise to acetic acid-2-C^{14} maintained at 85-95° C. according to
the procedure of Kharasch and Gladstone[5]. The apparatus was thoroughly
flushed out with purified water pumped nitrogen which had been passed
successively through tubes filled with drierite and ascarite and then
through a sulfuric acid bubbler. Eight cc. of acetic acid-2-C^{14} was
placed in the decomposition flask (B) and 2 cc. of a solution containing
approximately 0.5 g. of acetyl peroxide was placed in the side tube (A).
An aliquot of the acetyl peroxide solution was analyzed for peroxide
content immediately before use. The decomposition flask was placed in

an oil bath maintained at 85-95° C. and when temperature equilibrium had

been attained, the solution in tube (A) was slowly dropped into flask (B)

while constantly maintaining a slow stream of nitrogen, thus stirring the

solution in (B). Small gas bubbles immediately formed throughout the solu-

tion and the rate of gas evolution remained approximately constant until

all the solution in (A) had been added (3-5 hr). After the gas evolution

had ceased, the nitrogen sweep was continued for 2 hr. to insure complete

removal of gaseous reaction products. At the end of this time an aliquot

of the solution in (B) was analyzed for peroxide content, which was invari-

ably found to be zero. The water condenser (C) returned most of the acetic

acid-2-C^{14} vapors to the flask (B). Any acetic acid not condensed by the

water condenser was collected in the dry ice-isoprophyl alcohol cooled

trap (D), along with the methyl acetate. The acetic acid collected as a

solid film near the inlet tube while the methyl acetate collected as a

liquid in the bottom of the trap. The CO_2 was collected in the carbonate

free 2$\underline{N}$ NaOH in spiral bubbler (E) while the CH_4 (and any ethane, Co and

ethylene) was burned to CO_2 in the CuO packed furnace (G) which was main-

tained at   700°C. This CO_2 was collected in the 2$\underline{N}$ NaOH in spiral

bubbler (H). The solutions in the two NaOH bubblers were poured into an

equal volume of 2$\underline{N}$ NH_4NO_3 and excess $BaCl_2$ was added. The resulting

$BaCO_3$ was filtered, washed, and dried. The acetic acid-2-C^{14} in flask

(B) was steam distilled way from the succinic acid and was recovered as

sodium acetate. The residue in flask (B) was continuously ether extracted

for 16 hr., the ether evaporated, and the resulting crude succinic acid re-

crystallized from water, giving a final produce of M.P. 186-7°C. In a

representative run (run 2, Table III), 0.454 g. of acetyl peroxide gave

1.246 g. $BaCO_3$ from the CO_2, 0.963 g. $BaCO_3$ from the CH_4, and 0.2291 g.

succinic acid. In a blank run, omitting only the acetyl peroxide, less

than 1 mg. $BaCO_3$ was obtained from each of the NaOH bubblers. The above

figures give the following molar ratios: CO_2/acetyl peroxide = 1.64
                                                       CH_4/ acetyl peroxide = 1.27
                                                    succinic acid/acetyl peroxide = 0.50

Combustion and Counting of Samples

The reaction products and samples of the acetic acid-2-C^{14} used were

oxidized to CO_2 by a modified Van Slyke-Folch wet combusion method[17] in the

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(17) R. M. McCready and W. Z. Hassid, Ind. Eng. Chem. Anal. Ed., 14, 525 (1942).

---

apparatus shown in Figure 2. The sample and $\sim$ 0.3 g. KIO_3 were placed in

the combusion flask (B) and the vacuum was turned on, thus flushing the

system with air from which the CO_2 had been removed by the soda-lime

packed inlet tube (A). The bubbler was then filled with 2$\underline{N}$ carbonate free

NaOH (prepared from "Acculute" standard NaOH) with a syringe. Combustion

fluid[18] was then admitted through the funnel (C), and the flask was heated

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(18) The combustion fluid was prepared[17] by mixing 25 g. CrO_3, 5 g.
KIO_3, 167 ml. syrupy H_3PO_4 and 333 ml. fuming H_2SO_4 (20% free SO_3)
heating to 140-150°C. to effect solution, and allowing the solution
to cool, protected from water and dust.

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gently to start the reaction. The gentle heating was continued until

the CO_2 evolution subsided, after which the flask was heated more

strongly for a few minutes, with care to avoid SO_3 fumes caused by

overheating. The heating was discontinued and the sweep maintained for

about another hour to insure complete removal of the CO_2. The CO_2 was
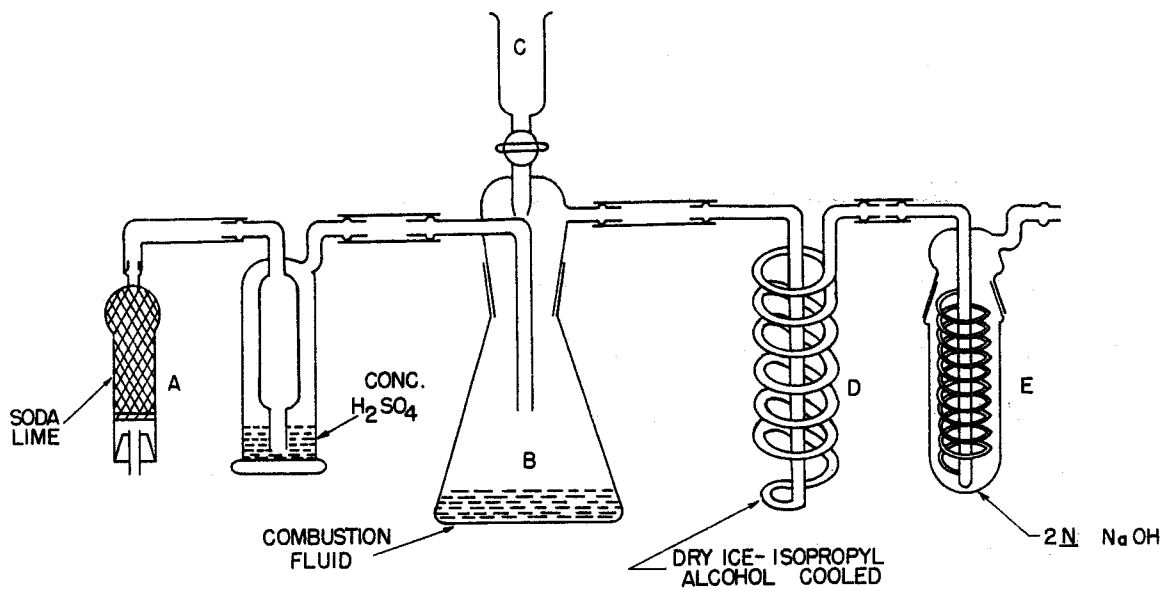
FIGURE 2

APPARATUS FOR WET COMBUSTION
OF ORGANIC COMPOUNDS

MU 1760

Fig. 2

collected as $BaCO_3$ as described above. The $BaCO_3$ samples were plated on thin aluminum disks and counted, using a thin window Geiger-Muller tube according to the procedure of Dauben, Reid, and Yankwich[19].

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(19) W. G. Dauben, J. Reid, and P. E. Yankwich, Anal. Chem., 19, 838 (1947)

Appropriate self-absorption corrections were made from standard curves.

Exchange of Methyl Acetate and Acetic Acid-2-C^{14}

Small tared thin walled glass bulbs were filled with inactive methyl acetate and acetic acid-2-C^{14}. The bulbs were sealed off and reweighed and placed in a trap on a vacuum line along with an iron slug. After evacuation, the bulbs were broken by raising the slug with a magnet, and dropping it on the bulbs. The acid and ester were then quantitatively distilled into a container which was closed off by a stopcock which was clamped in place. The entire vessel was put in a steam bath and heated for 5 hrs. The mixture was then back distilled in vacuo into a spiral trap. The mixture in the trap was then slowly vaporized into a CO_2 free N_2 stream, which was led in turn through a spiral bubbler filled with ethanolamine maintained at 90-95°C., a drying tube tightly packed with glass wool to remove any entrained ethanolamine, the CuO packed furnace at 700°, and a spiral bubbler filled with 2N NaOH, from which the CO_2 was obtained as $BaCO_3$. From a mixture of 0.1499 g. acetic acid-2-C^{14} and 0.3466 g. methyl acetate, 1.561 g. $BaCO_3$ was obtained, during the first 15 hrs., 0.091 g. $BaCO_3$ during the next 24 hrs., and 0.016 g. $BaCO_3$ during the next 26 hrs. This corresponds to 56.3% yield based on methyl

acetate. The $BaCO_3$ activity was 19.7 dis./min./mg.C, while the activity

of the $C^{14}H_3COCH$ used was 2.60 x 10^4 dis./min./mg.C.

Hydrolysis of Methyl Acetate

A bulb containing 0.1528 g. CH_3COOCH_3 was broken in vacuo and the contents

distilled into a vessel containing 2 cc. 2N NaOH. The vessel was closed off,

the stopcock clamped in place, and heated on the steam bath two hrs. The

methyl alcohol and water were then distilled back into a spiral trap,

leaving a residue of dry sodium acetate and sodium hydroxide. The methyl

alcohol-water solution was vaporized into a stream of CO_2 free N_2 and

passed through the CuO packed furnace at   700°C. The resulting CO_2 was

absorbed in a bubbler filled with 2N NaOH, and collected as $BaCO_3$, giving

0.395 g. (97.0%). The sodium acetate-sodium hydroxide residue was acidified

with H_2SO_4 and steam distilled. The acetic acid in the distillate required

20.00 cc. 0.1000 N NaOH for neutralization, corresponding to a yield of

97.0% acetic acid. When this procedure was applied to the material from

run 6 which had come through the ethanolamine procedure, 0.180 g.

(0.912 millimoles) $BaCO_3$ was obtained, while only 4.43 cc. 0.1000 N NaOH

(0.433 millimoles) was required to neutralize the acetic acid. When the

purified methyl acetate from run 7 was hydrolyzed in this manner, 0.691 g.

(3.50 millimoles) $BaCO_3$ was obtained, from the methyl alcohol, and 36.00 cc.

0.1000 N NaOH (3.60 millimoles) was required to neutralize the acetic acid.

Separation of Acetic Acid from Methyl
Acetate by Washing with Sodium Bicarbonate

Bulbs containing 0.3741 g. methyl acetate and 0.3641 g. acetic acid-2-C^{14}

were broken in vacuo and the contents distilled into a vessel containing

10 cc. of 10% NaHCO$_3$ solution. The vessel was closed off and vigorously

shaken for a few seconds. The volatile material was then back-distilled

into a spiral trap, from which it was later volatilized into a N$_2$ stream

and oxidized in the CuO packed furnace. The CO$_2$ was collected as BaCO$_3$,

wt. = 2.731 g., 91.4% based on methyl acetate.