UCRL 573
Cy. 2

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

BERKELEY, CALIFORNIA

Copy No. 2

UCRL-573

UNCLASSIFIED

Unclassified Distribution

UNIVERSITY OF CALIFORNIA

Radiation Laboratory

Contract No. W-7405-eng-48

A PRELIMINARY REPORT ON THE MECHANISM OF THE DECOMPOSITION OF DIACETYL PEROXIDE IN ACETIC ACID

A. J. Fry, B. M. Tolbert and Melvin Calvin

December 29, 1949

Berkeley, California

INSTALLATION	No. of Copies
Argonne National Laboratory	8
Armed Forces Special Weapons Project	1
Atomic Energy Commission, Washington	2
Battelle Memorial Institute	1
Brookhaven National Laboratory	8
Bureau of Medicine and Surgery	1
Bureau of Ships	1
Carbide & Carbon Chemicals Corp. (K-25)	4
Carbide & Carbon Chemicals Corp. (Y-12)	4
Chicago Operations Office	1
Cleveland Area Office	1
Columbia University (Dunning)	1
Columbia University (Failla)	1
Dow Chemical Company	1
General Electric Company, Richland	6
Idaho Operations Office	1
Iowa State College	2
Kansas City	1
Kellex Corporation	2
Knolls Atomic Power Laboratory	4
Los Alamos	3
Mallinckrodt Chemical Works	1
Massachusetts Institute of Technology (Gaudin)	1
Massachusetts Institute of Technology (Kaufmann)	1
Mound Laboratory	3
National Advisory Committee for Aeronautics	2
National Bureau of Standards	2
Naval Radiological Defense Laboratory	2
NEPA Project	2
New Brunswick Laboratory	1
New York Operations Office	3
North American Aviation, Inc.	1
Oak Ridge National Laboratory	8
Patent Advisor, Washington	1
Rand Corporation	1
Sandia Base	1
Sylvania Electric Products, Inc.	1
Technical Information Branch, ORE	15
U. S. Public Health Service	1
UCLA Medical Research Laboratory (Warren)	1
University of California Radiation Laboratory	5
University of Rochester	2
University of Washington	1
Western Reserve University (Friedell)	2
Westinghouse	4
Total	116

Information Division
Radiation Laboratory
Univ. of California
Berkeley, California

A PRELIMINARY REPORT ON THE MECHANISM OF THE DECOMPOSITION OF DIACETYL PEROXIDE IN ACETIC ACID*

By

A.J. Fry, B.M. Tolbert and Melvin Calvin

ABSTRACT

December 29, 1949

(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 those reagents were heated at 100° for five hours.

To be presented at Brookhaven conference on "Tracers in Organic Reaction Mechanisms", January 19-20, 1950.

---

* The work described in this paper was sponsored by the Atomic Energy Commission.

A PRELIMINARY REPORT ON THE MECHANISM OF THE DECOMPOSITION OF DIACETYL PEROXIDE IN ACETIC ACID*

By

A.J. Fry, B.M. Tolbert and Melvin Calvin

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

The decomposition of diacetyl peroxide in aliphatic acids has been reported (1) to result in the formation of succinic acid or its substitution derivatives, methane, carbon dioxide and some methyl acetate. The mechanism proposed for this reaction was the following:

$$(CH_3COO)_2 \xrightarrow{\Delta} CO_2 + CH_3\cdot + CH_3COO\cdot$$

$$CH_3\cdot + CH_3COOH \longrightarrow CH_4 + \cdot CH_2COOH$$

$$2\cdot CH_2COOH \longrightarrow HOOCCH_2CH_2COOH$$

$$2\ CH_3COO\cdot \longrightarrow CH_3COOCH_3 + CO_2$$

$$(CH_3COO)_2 + CH_3COO\cdot \longrightarrow CH_3COOCH_3 + CO_2 + CH_3COO\cdot$$

---

* To be presented at Brookhaven Conference on "Tracers in Organic Reaction Mechanisms", January 19-20, 1950.

** The work described in this paper was sponsored by the Atomic Energy Commission.

(1) Kharasch and Gladstone, J. Am. Chem. Soc. 65, 15 (1943)

An examination of the proposed mechanism reveals that it could be very easily checked using C^{14}-labeled compounds. For instance, if unlabeled diacetyl peroxide and acetic acid-2-C^{14} were used, the above mechanism would result in the formation of unlabeled carbon dioxide, methane and methyl acetate, and labeled succinic acid in which each methylene group would have the same specific activity as the methyl group of the acetic acid.

Diacetyl Peroxide-Acetic Acid Exchange Studies: - In order to check the mechanism of this reaction as outlined above it was first necessary to examine the possibility of exchange between acetic acid and diacetyl peroxide. This was done by dissolving solid unlabeled diacetyl peroxide in acetic acid-2-C^{14} and allowing the solution to stand first for one hour at room temperature and later for one week at room temperature followed by six hours at 53° C. The peroxide titer 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. The final aqueous and carbon tetrachloride solutions contained pure acetic acid and diacetyl peroxide, respectively.

Preliminary work had shown that the above procedure was sufficient to separate the two compounds from each other quantitatively.

The diacetyl peroxide in the carbon tetrachloride solution 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 counting results given in Table I show that within the experimental error of counting, none of the activity in the acetic acid was found in the diacetyl peroxide. The fact that the recovered acetic acid had a lower specific activity than the original acetic acid is probably due to some non-reversible hydrolysis of the diacetyl peroxide during the separation procedure.

TABLE I

Diacetyl Peroxide-Acetic Acid Exchange Studies

Exchange Conditions	Specific Activity, c/m/mg. CH_3COONa			
	Original		Recovered	
	Acetic Acid	Diacetyl Peroxide	Acetic Acid	Diacetyl Peroxide
1 hr. at 23°C	273	0	258	0.0
1 wk. at 23° C followed by 6 hr. at 50° C	288	0	239	0.85

Decomposition of Diacetyl Peroxide in Acetic Acid: - Diacetyl peroxide dissolved in acetic acid-2-C^{14} was decomposed by adding it dropwise to

acetic acid maintained at 85-95° C according to the procedure of Kharasch and Gladstone (1). The reaction 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-isopropyl alcohol bath, a spiral bubbler filled with 2 M 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 reaction 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 and recrystallization from water after evaporation of the ether. The carbon dioxide from the two sodium hydroxide bubblers was precipitated and weighed as barium carbonate.

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

TABLE II

Molar Ratio of Products Obtained in the Decomposition of Diacetyl Peroxide in Acetic Acid

Moles X/Moles Diacetyl Peroxide

Experiment / x =	Beginning Acetic Acid	Carbon Dioxide	Methane	Succinic Acid
Kharasch	34.7	1.53	1.47	0.50
This work***	37	1.54	1.13	0.40

The relative specific activities of the various reaction products are shown in Table III expressed as precentages of the specific activity of the methyl group of the acetic acid used. All of the products were burned to carbon dioxide and counted as barium carbonate.

The methyl acetate in Runs 4, 5 and 6 was separated from the acetic acid with which it was mixed in the cold trap, by bubbling oxygen through the trap as it warmed up and on through a spiral trap filled with diethanolamine at 90° C. Entrained diethanolamine was removed with a glass wool filter and the methyl acetate in the oxygen stream was passed

*** Data averaged from 8 runs.

through a furnace in Runs 4 and 5, and a cold trap in Run 6 to condense out the methyl acetate. In Run 7 the methyl acetate was separated from the acetic acid by washing with sodium bicarbonate. The purified methyl acetate from Runs 6 and 7 was hydrolyzed with sodium hydroxide and the methyl alcohol and sodium acetate were burned and counted as barium carbonate.

In order to test the possibility of exchange between the acetic acid and methyl acetate and to test the diethanolamine purification procedure described above, inactive methyl acetate and acetic acid-2-C^{14} were mixed and allowed to stand both at room temperature and at 100° C for five hours. The methyl acetate was then separated from the acetic acid by bubbling through diethanolamine as described above. The methyl acetate which came through the bubbler was burned and the resulting carbon dioxide was counted as barium carbonate. The activity found in the most active methyl acetate sample corresponded to 0.45% of the amount calculated for complete exchange.

DISCUSSION

From the data in Table III it can be concluded that within our experimental error the succinic acid methylene groups have the same specific activity as the acetic acid methyl group and that the carbon dioxide is inactive. These results are in complete agreement with the mechanism proposed by Kharasch and Gladstone. However, the presence of appreciable amounts of activity in the methyl acetate was not predicted by the proposed mechanism. The low value and great variability of the specific activity of the methane seem to indicate that some unknown factor may be responsible for this effect.

However, the presence of such a large amount of activity and its unequal distribution between the two methyl groups in the methyl acetate seems to indicate quite conclusively that this compound cannot be formed exclusively in the manner proposed by Kharasch and Gladstone.

At the present time, we are unable to present a mechanism by which the data presented can be satisfactorily explained without postulating more than a single source of methylacetate. Obviously, the data are as yet quite incomplete and further work is in progress in an attempt to throw light on the path by which activity gets into the methyl acetate and methane. It should be pointed out that the relative specific acitvity of the methane is an upper limit on the amount of exchange between the acetic acid and the diacetyl peroxide

TABLE III

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

Run	Acetic Acid Used[1]	Diacetyl Peroxide[1] Used	CO_2 Produced	CH_4 Produced	Succinic Acid Produced[1]	Acetic[1] Acid Recover.	Methyl Acetate Produced	
1	100[2]	0.00	0.00 ± 0.1	0.07 ± 0.1	97.8 ± 2.0	101.5 ± 2.0	< 28	
2	100	0.00	0.01 ± 0.1	0.16 ± 0.1	93.7 ± 2.0	103.0 ± 2.0		
3[3]	100	0.00	0.06 ± 0.1	0.60 ± 0.1	--	100.0 ± 2.0	< 28	
4[3]	100	0.00	0.00 ± 0.1	0.34 ± 0.1	--	99.6 ± 2.0	< 9.1	
5	100	0.00	0.00 ± 0.1	1.64 ± 0.1	97.2 ± 2.0	99.8 ± 2.0	< 12.0	
							Acetate[1] fragment	Alcohol fragment
6	100	0.00	0.00 ± 0.1	2.50 ± 0.1	--	98.0 ± 2.0	32.5 ± 0.6	3.19 ± 0.1
7[3]	100	0.00	0.07 ± 0.1	0.36 ± 0.1	--	103.4 ± 2.0	13.5 ± 0.3	2.71 ± 0.1

1 Methyl or methylene group only.

2 Actual specific activity = $5.20 \pm 0.11 \times 10^4$ or $9.96 \pm 0.20 \times 10^3$ d/m/mg CH_3 -carbon

3 Ratio of acetic acid to diacetyl peroxide used = ~8 instead of 37

under the conditions of the decomposition, since its source must be the methyl group of either the acetic acid or the diacetyl peroxide.

EXPERIMENTAL

Diacetyl peroxide[1] was prepared according to the method of Gamborjan (2) as modified by Kharasch, McBay and Urry (3). 20.0 g. of acetic anhydride, 10.0 g. of sodium peroxide and 100 cc. of diethyl ether were mixed together in an Erlenmeyer flask and cooled to -15° C. 35 g. of crushed ice was gradually added over a 10 minute period with vigorous shaking. The ether solution was separated off, dried with calcium chloride and allowed to stand several hours in a dry ice-isopropyl alcohol bath. The acetyl peroxide crystallized out in long white needles, and the ether superntant 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. The dry diacetyl peroxide was dissolved in the solvent it was to be used in as soon as possible to minimize the explosive possiblilities.

The peroxide solutions were analyzed by the method of Kokatnur

---

(2) Gamborjan, Ber. 42, 4010 (1909)

(3) Kharasch, McBay and Urry, J. Org. Chem. 10, 397 (1945)

and Jelling (4). The peroxide sample was dissolved in 99% isopropyl alcohol and one cc. each of glacial acetic acid and saturated potassium iodide was added. The solution was heated almost to boiling and maintained at that temperature for about five minutes, and then titrated without cooling with standard $Na_2S_2O_3$. The oxygen blank is negligible with this procedure.

The acetic acid used was specially purified by slowly freezing out about half of a sample of glacial acetic acid and distilling the crystals so obtained. The middle half of the distillate was used. The acetic acid-2-C^{14} was prepared by allowing 50 cc of the glacial acetic acid prepared as described above to stand for 72 hours with 0.038 g. of 5.29 μc/mg. sodium acetate-2-C^{14} to effect complete exchange and distilling the resulting active acetic acid. The sodium acetate-2-C^{14} was prepared by carbonation of the Grignard reagent prepared from methyl iodide-C^{14} (5).

The reaction products were burned to carbon dioxide over hot copper oxide or by a modified Van Slyke-Folch wet combustion method (6). The carbon dioxide was absorbed in 2 M carbonate free

---

(4) Kokatnur and Jelling, J. Am. Chem. Soc. 63, 1432 (1941)

(5) Tolbert, J. Biol. Chem. 173, 205 (1948)

(6) McCready and Hassid, Ind. Eng. Chem., Anal. Ed. 14, 525 (1942)

sodium hydroxide. An equal volume of 2M ammonium nitrate was added and the carbonate was precipitated as barium carbonate by adding 1M barium nitrate. The barium carbonate was plated on aluminum disks using thin window Geiger Müller tubes (7). The precision of the counting data is indicated in Table III.

---

(7) Dauben, Reid and Yankwich, Anal. Chem. 19, 828 (1947)

SUMMARY

(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 those reagents were heated at 100° for five hours.