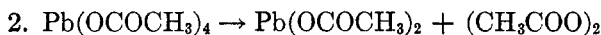
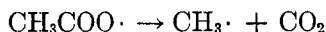
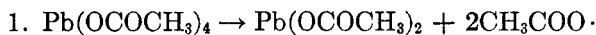


REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XVIII.  
DECOMPOSITION OF DIACETYL PEROXIDE IN *vic*-GLYCOLS

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It has been postulated (1) that lead tetraacetate decomposes, when heated in solvents, to give lead diacetate and diacetyl peroxide or lead acetate and free acetoxy (and/or free methyl) radicals:



Since this hypothesis postulates either the formation of diacetyl peroxide or fragments presumably similar to those assumed in the decomposition of diacetyl peroxide (2), the decomposition of lead tetraacetate and of diacetyl peroxide in acetic acid and diisopropyl ether was investigated (3). Because the reaction products were different in the two cases, it was concluded that although some free radicals (methyl and acetoxy) are formed in the decomposition of lead tetraacetate in these solvents, the reaction mechanism in the case of lead tetraacetate is not dependent upon either of the mechanisms (1 and 2) postulated above.

Further to confirm that when heated in solvents lead tetraacetate does not decompose into fragments similar to those formed from diacetyl peroxide, the decomposition of diacetyl peroxide in *vic*-glycols (2,3-butanediol and hydrobenzoin) was investigated.

RESULTS

The results obtained by the decomposition of diacetyl peroxide in 2,3-butanediol and hydrobenzoin are given in Tables I and II. Because of the experimental difficulties involved in the separation of acetoin (Table I) and in separating benzil, benzoin, and hydrobenzoin (Table II), three compounds whose physical properties are quite similar (solubility in solvents and melting points), our balance sheets for the entire reaction are not as adequate as in other reactions involving the decomposition of diacetyl peroxide. Nevertheless, the results are quite unambiguous. The *vic*-glycols when treated with diacetyl peroxide give the corresponding hydroxy ketones and diketones. The aldehydes or ketones, which are formed in such excellent yields when lead tetraacetate is used, are formed in insignificant quantities when diacetyl peroxide is used.

The 2,3-butanediol used in experiment 2 (Table I) had 4.6% of the hydroxyl hydrogen atoms replaced by deuterium. Yet, the methane produced in the reaction contained less than 0.01% of deuterium.

When pinacol, dissolved in acetic acid, is treated with acetyl peroxide, it is recovered unchanged, while the acetic acid is converted to succinic acid.

TABLE I  
THE DECOMPOSITION OF DIACETYL PEROXIDE IN 2,3-BUTANEDIOL

REACTANTS	MOLES	MOLES
2,3-Butanediol.....	6.4	7.3
Diacetyl peroxide.....	1.0	1.0
PRODUCTS	MOLES/MOLE ACETYL PEROXIDE	MOLES/MOLE ACETYL PEROXIDE
Carbon dioxide.....	1.0	1.3
Carbon monoxide.....	0.0	0.0
Methane (contains small percentage of ethane).....	0.97	1.3
Methyl acetate.....	0.0	0.0
Acetic acid.....	0.74	0.77
Acetoin.....	0.39	0.26
Biacetyl.....	0.18	0.13
Acetaldehyde.....	0.01 <sub>2</sub>	0.00 <sub>2</sub>

TABLE II  
THE DECOMPOSITION OF DIACETYL PEROXIDE IN HYDROBENZON

REACTANTS	MOLES
Diacetyl peroxide.....	1.0
Hydrobenzoin.....	1.08
<i>t</i> -Butyl alcohol.....	6.0
PRODUCTS	MOLES/MOLE ACETYL PEROXIDE
Carbon dioxide.....	1.04
Carbon monoxide.....	0.0
Methane.....	0.71
Ethane.....	0.12
Acetic acid.....	0.74
Methyl acetate.....	0.06
Benzoin.....	0.14
Benzil.....	0.18
Benzaldehyde.....	trace
Recovered hydrobenzoin.....	0.58

#### DISCUSSION

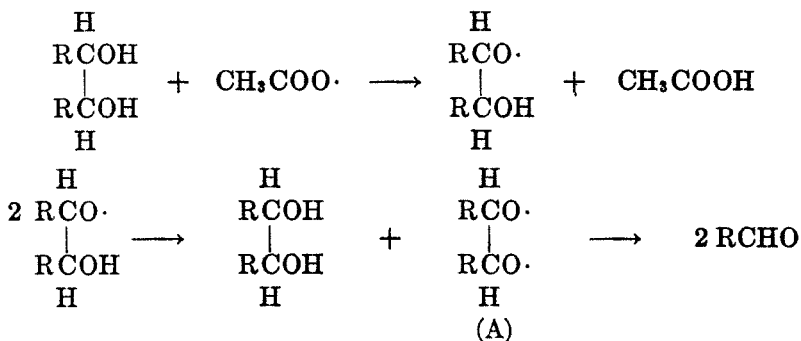
The fact that diacetyl peroxide when heated in *vic*-glycols does not break the carbon-to-carbon bond of the glycols, but forms the corresponding keto alcohols and diketones, invalidates, in our estimation, the hypothesis that in the oxidation of *vic*-glycols lead tetraacetate functions by virtue of a *primary* breakdown into lead acetate and free acetoxy radicals, or lead acetate and acetyl peroxide (1).

There is another fundamental difference between lead tetraacetate and acetyl peroxide insofar as the reactions with glycols and alcohols are concerned. The

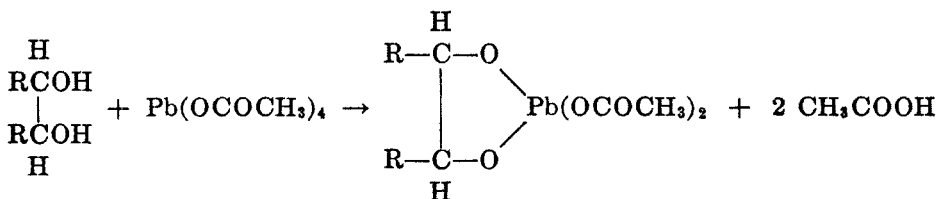
difference is in the point of the initial attack of these reagents. Acetyl peroxide attacks the hydrogen atom attached to the carbon atom holding the hydroxyl group, whereas lead tetraacetate attacks the hydroxyl hydrogen atoms. These facts help to explain why acetyl peroxide attacks acetic acid solutions of *vic*-glycols such as hydrobenzoin or 3,4-butanediol more readily than glycols of the type of pinacol (which it does not attack in acetic acid solution), whereas lead tetraacetate attacks all of these *vic*-glycols with equal ease.

Furthermore, there is no evidence that the free radicals, formed by the decomposition of diacetyl peroxide in alcohols, ever attack the hydrogen atom of the hydroxyl group. Thus, acetyl peroxide attacks isopropyl alcohol with greater ease than *t*-butyl alcohol, indicating an attack on different atoms in the two molecules. Furthermore, deuterium tracer experiments have shown that deuterium atoms attached to the oxygen atoms in 2,3-butanediol are not attacked by the free radicals formed by the decomposition of diacetyl peroxide. Similar results were obtained with deuterium tracer experiments with *t*-butyl alcohol and isopropyl alcohol in which the deuterium was attached to the oxygen atom. The methane formed in all cases contained less than 0.01% of deuterium. On the other hand, the methane formed by decomposition of diacetyl peroxide in isopropanol in which some of the hydrogen atoms on the carbon atoms carrying the hydroxyl groups were replaced by deuterium, gave a mixture of methane and deuteromethane containing approximately the statistically calculated amount of deuterium (4).

Our evidence is thus contrary to the hypothesis of Waters (1) that free radicals are intermediates in the oxidation of *vic*-glycols.



For the reasons here cited, as well as other reasons (5), we favor the hypothesis (6) that oxidation of *vic*-glycols proceeds through the formation of a cyclic lead compound



which breaks down to give lead acetate and two molecules of the aldehyde. It is purely a matter of taste whether one wishes to postulate the transient existence during this breakdown of a biradical (A), which at once decomposes into two molecules of aldehyde or ketone.

The mechanism of the decomposition of diacetyl peroxide in *vic*-glycols may be postulated in a manner similar to that of the induced decomposition of benzoyl peroxide in alcohols (7).

1.  $\text{CH}_3\text{CO}_2\text{O}_2\text{CCH}_3 \rightarrow \text{CH}_3\text{CO}_2\cdot \text{CH}_3\cdot + \text{CO}_2$
2.  $\text{CH}_3\text{CO}_2\cdot \rightarrow \text{CH}_3\cdot + \text{CO}_2$
3.  $2\text{CH}_3\text{CO}_2\cdot \rightarrow \text{CH}_3\text{CO}_2\text{CH}_3 + \text{CO}_2$
4.  $\text{CH}_3\cdot + \text{CH}_3\text{CO}_2\text{O}_2\text{CCH}_3 \rightarrow \text{CH}_3\text{CO}_2\text{CH}_3 + \text{CH}_3\text{CO}_2\cdot$
5.  $\text{CH}_3\cdot + \text{CH}_3\text{CO}_2\text{O}_2\text{CCH}_3 \rightarrow \text{C}_2\text{H}_6 + \text{CH}_3\text{CO}_2\cdot + \text{CO}_2$
6.  $\text{CH}_3\cdot + \text{RCH}(\text{OH})\text{CH}(\text{OH})\text{R} \rightarrow \text{CH}_4 + \cdot\text{C}(\text{OH})\text{RCH}(\text{OH})\text{R}$
7.  $\cdot\text{C}(\text{OH})\text{RCH}(\text{OH})\text{R} + \text{CH}_3\text{CO}_2\text{O}_2\text{CCH}_3 \rightarrow \text{RCH}(\text{OH})\text{C}(\text{OH})\text{-(OCOCH}_3\text{)R} + \text{CH}_3\cdot + \text{CO}_2$
8.  $\text{RCH}(\text{OH})\text{C}(\text{OH})\text{(OCOCH}_3\text{)R} \rightarrow \text{RCH}(\text{OH})\text{COR} + \text{CH}_3\text{CO}_2\text{H}$
9.  $\text{CH}_3\cdot + \text{RCH}(\text{OH})\text{COR} \rightarrow \text{CH}_4 + \cdot\text{C}(\text{OH})\text{(COR)R}$
10.  $\cdot\text{C}(\text{OH})\text{(COR)R} + \text{CH}_3\text{CO}_2\text{O}_2\text{CCH}_3 \rightarrow \text{RCOC}(\text{OH})\text{(OCOCH}_3\text{)R} + \text{CH}_3\cdot + \text{CO}_2$
11.  $\text{RCOC}(\text{OH})\text{(OCOCH}_3\text{)R} \rightarrow \text{RCOCOR} + \text{CH}_3\text{CO}_2\text{H}$

Reactions 3, 4, and 5 are side reactions. Reactions 6 and 7 and corresponding reactions 9 and 10 constitute the main reaction chain.

It is noteworthy, that in all induced decompositions of diacetyl peroxide about equimolar quantities of acetic acid and methane are formed; while in the non-induced decomposition reactions of diacetyl peroxide small amounts, if any, of acetic acid are formed.<sup>1</sup>

#### EXPERIMENTAL

*Decomposition of acetyl peroxide in 2,3-butanediol.* A solution of acetyl peroxide (36.5 g., 0.31 mole) in 2,3-butanediol<sup>2</sup> (180 g., 2 moles,  $n_D^{20}$  1.4363) was dropped into a flask held at 95°. A gas-collector train of the type previously described (8) was used to collect the carbon dioxide (13.5 g., 0.31 mole) and the methane (7.5 l., 0.3 mole). The reaction mixture was distilled and separated into the following fractions: 1. a low-boiling fraction containing biacetyl, acetic acid, and traces of acetaldehyde; 2. a medium-boiling fraction containing acetic acid and acetoin; 3. the bulk of the 2,3-butanediol containing some acetoin. The

<sup>1</sup> Except with molecules containing very active hydrogen atoms, such as aldehydes, in which the hydrogen atoms can be removed by free acetoxy radicals.

<sup>2</sup> The 2,3-butanediol (90% *meso*, 10% *dextro*) was obtained through the kindness and generosity of the Northern Regional Research Laboratory of the Department of Agriculture at Peoria, Illinois.

acetic acid was determined by titration of an aliquot with 0.1 *N* sodium hydroxide. The acetaldehyde was determined quantitatively by precipitation as the methone derivative (9) which melted at 139.5–140.5°. The melting point of the methone derivative of acetaldehyde (9) given in the literature is 135–140°.

The acetoin (Fraction 2) and the biacetyl (Fraction 1) were determined quantitatively by precipitation with 2,4-dinitrophenylhydrazine (10). The results thus obtained were in close agreement with those calculated from the refractive indices of the various fractions. The biacetyl and acetoin were further identified by reaction with phenylhydrazine. Biacetyl formed a bis-phenylhydrazone which melted at 244–245°. Acetoin formed a phenyllosazone which melted at 247–248°. The two compounds, however, are identical, and they did not depress the melting point of each other. The recorded melting point of the bis-phenylhydrazone of biacetyl is 243°.

*Decomposition of diacetyl peroxide in 2,3-butanediol containing deuterium.* The method employed for the decomposition of the diacetyl peroxide was the same as previously described, except that the 2,3-butanediol contained 4.6% deuterium in place of hydrogen atoms in the hydroxyl groups. The deuterio-2,3-butanediol was prepared by allowing 2,3-butanediol to equilibrate with heavy water for 24 hours. The glycol was then dried with calcium sulfate and distilled at reduced pressure. The partially deuterated 2,3-butanediol ( $n_D^{20}$  1.4351) boiled at 91–92° at 19 mm. The amount of deuterium was determined by allowing the glycol to react with methylmagnesium iodide in butyl ether. The methane produced was burned over a hot platinum wire, and the density of the water was determined by the flotation temperature of a calibrated quartz float (4). The amount of deuterium in the methane from the acetyl peroxide decomposition was determined in a similar fashion. The amount of deuterium in the methane formed by the decomposition of diacetyl peroxide was less than 0.01%. The reaction mixture was distilled as previously described. The amounts of acetoin and biacetyl formed in the reaction were determined, however, by the empirical method of Langlykke and Peterson (11). The agreement of the two experiments was very good (see Table I).

*Decomposition of diacetyl peroxide in hydrobenzoin.* The diacetyl peroxide and the hydrobenzoin were dissolved in *t*-butyl alcohol; otherwise the procedure was the same as described previously for the decomposition of the diacetyl peroxide in 2,3-butanediol.

The reaction mixture was subjected to fractional crystallization first from the solvent and then from ethyl ether and from alcohol. The course of the fractionation was followed by noting changes in the melting points of the fractions when these were mixed with authentic samples of benzoin, benzil, and hydrobenzoin. As a check on the separation of the mixtures the precipitation of 2,4-dinitrophenylhydrazones (10) was undertaken. The results of these experiments were in fair agreement with those obtained by the fractional crystallizations. Benzil was identified by the melting point 125–126° of 2,3-diphenylquinoxaline prepared from it and *o*-phenylenediamine. The melting point given in the literature is 126.2°. The 2,4-dinitrophenylhydrazone of benzoin melted at 235–236°, and it did not depress the melting point of an authentic sample. The benzaldehyde was identified by conversion to its 2,4-dinitrophenylhydrazone. The material melted at 235–237°, and it did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of benzaldehyde.

#### SUMMARY

1. The reaction of acetyl peroxide with 2,3-butanediol gave carbon dioxide, methane, acetic acid, acetoin, biacetyl, and only a trace of acetaldehyde.
2. Deuterium tracer experiments have demonstrated that the hydrogen atom attached to the oxygen atom is not attacked by the free radical fragments formed in the decomposition of diacetyl peroxide.
3. The reaction of acetyl peroxide with hydrobenzoin in *t*-butyl alcohol so-

lution gave carbon dioxide, methane, methyl acetate, acetic acid, benzoin, benzil, and only a trace of benzaldehyde.

4. The bearing of these results on the mechanism of the action of lead tetraacetate on *vic*-glycols is discussed.

5. A mechanism for the decomposition of acetyl peroxide in glycols is proposed.

CHICAGO 37, ILL.

#### REFERENCES

- (1) WATERS, "The Chemistry of Free Radicals," Oxford University Press (1948); see also FIESER AND CHANG, *J. Am. Chem. Soc.*, **64**, 2043 (1942); FIESER, CLAPP, AND DAUDT, *J. Am. Chem. Soc.*, **64**, 2053 (1942).
- (2) KHARASCH AND GLADSTONE, *J. Am. Chem. Soc.*, **65**, 15 (1943).
- (3) KHARASCH, FRIEDLANDER, AND URRY, Unpubl. work.
- (4) This work will be discussed in greater detail in a forthcoming publication by Kharasch, Rowe, and Urry.
- (5) KHARASCH, FRIEDLANDER, AND URRY, Unpubl. work.
- (6) CRIEGEE, KRAFT AND RANK, *Ann.*, **507**, 159 (1933).
- (7) CASS, *J. Am. Chem. Soc.*, **68**, 1976 (1946); BARTLETT AND NOZAKI, *J. Am. Chem. Soc.*, **69**, 2299 (1947).
- (8) KHARASCH, MCBAY, AND URRY, *J. Org. Chem.*, **10**, 394 (1945).
- (9) WEINBERGER, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).
- (10) KHARASCH AND COOPER, *J. Org. Chem.*, **10**, 48 (1945). FERRANTE AND BLOOM, *Am. J. Pharmacy*, **105**, 381 (1933).
- (11) LANGLYKKE AND PETERSON, *Ind. Eng. Chem., Anal. Ed.*, **9**, 163 (1937).