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REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXVI. COMPARISON OF THE REACTIONS OF LEAD TETRAACETATE AND ACETYL PEROXIDE WITH ACETIC ACID AND ISOPROPYL ETHER[1]

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It has been postulated (1) that, when heated in solution, lead tetraacetate decomposes monomolecularly to yield lead diacetate and acetyl peroxide or free acetoxy and/or free methyl radicals.

(a) $Pb(O_2CCH_3)_4 \rightarrow Pb(O_2CCH_3)_2 + (CH_3CO_2)_2$
(b) $Pb(O_2CCH_3)_4 \rightarrow Pb(O_2CCH_3)_2 + 2\ CH_3CO_2\cdot$
(c) $CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$

Several observations, however, cast doubt on the sufficiency of this postulate as an explanation of lead tetraacetate reaction. For one thing, Schall (2) has found that the thermal decomposition of lead tetraacetate in a sealed tube is not appreciable below 180°, and that decomposition in dilute aqueous acetic acid begins somewhere between 140 and 180°. It is well known that decomposition takes place readily at much lower temperatures in many organic solvents, and furthermore that the rate of decomposition varies considerably with the solvent.

The mode of decomposition suggested would also imply that lead tetraacetate and acetyl peroxide serve as sources of the same free radicals and should therefore react with other organic compounds in approximately the same proportions to yield the same products.

According to Fieser and Chang (3), 2-methyl-1,4-naphthoquinone gives an optimum yield (*ca.* 50%) of 2,3-dimethyl-1,4-naphthoquinone when treated with approximately four equivalents of lead tetraacetate. Fieser and Oxford (4), however, found that the optimum yield (*ca.* 50%) of the same product was obtained by treating 2-methyl-1,4-naphthoquinone with approximately one equivalent of acetyl peroxide. Moreover it has been shown in this laboratory (5) that, whereas treatment of a vicinal glycol (2,3-butanediol, hydrobenzoin) with lead tetraacetate results in cleavage of a carbon-to-carbon bond with formation of an aldehyde (acetaldehyde, benzaldehyde), treatment with acetyl peroxide leads to formation of the corresponding hydroxy ketone and diketone (acetoin, biacetyl; benzoin, benzil).

Although various hydrogen donors [*e.g.*, malonic esters, Fieser, *et al.*, (3)] have been used as "promoters" in lead tetraacetate reactions, there has, apparently, been no adequate investigation of the possible interaction of lead tetraacetate with acetic acid, a solvent commonly employed for such reactions (6). That

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[1] This paper was presented in part at the 107th meeting of the American Chemical Society, Cleveland, Ohio, April, 1944.

such interaction is possible is suggested by the formation of *o*-acetylglycolic anhydride through the action of lead tetraacetate on acetic anhydride (7), and by the presence of CH_3COOCH_2COO— and CH_3COO— groups in the product of reaction of lead tetraacetate and cyclopentadiene (8).

The present study was undertaken for the purposes of investigating the interaction of lead tetraacetate and acetic acid and of making further comparisons of corresponding reactions of lead tetraacetate and acetyl peroxide.

RESULTS OF PRESENT STUDY

In Table I are included data from the present study on the decomposition of lead tetraacetate in acetic acid, and, for comparative purposes, data from the previous study of Kharasch and Gladstone (9) on the decomposition of acetyl peroxide in acetic acid. It is obvious on casual inspection that there are marked differences in the reaction products obtained with the two reagents. With lead tetraacetate the principal product (other than fragments of the reagent itself) is acetoxyacetic acid; with acetyl peroxide it is succinic acid. Methylene diacetate appears as a product of the lead tetraacetate reaction, but not of the acetyl peroxide reaction. The reverse is true of methyl acetate. The amounts of carbon dioxide and methane liberated are significantly greater (four- to five-fold) in the acetyl peroxide than in the lead tetraacetate reactions.

To throw further light on the nature of the reaction of lead tetraacetate with acetic acid the rate of disappearance of the tetraacetate was determined in several experiments.[2] Analysis of the kinetic data indicates that the decomposition follows no simple reaction order. The general picture suggests that the products of the acetic acid-lead tetraacetate reaction react more rapidly with lead tetraacetate than does acetic acid itself. Confirmation of this surmise was obtained in runs in which acetoxyacetic acid or methylene diacetate were added to the initial reaction mixtures. In such cases the general character of the reaction remained substantially the same, but the rate of disappearance of the tetraacetate was increased. The data of column 6, Table I were derived from one such run.

In Table II are included data from the present study on the decomposition of lead tetraacetate in isopropyl ether, together with data from a previous study of Kharasch and Fineman (10) on the decomposition of acetyl peroxide in the same solvent. There is not the marked difference in reaction products that characterizes the acetic acid reactions, but there are significant differences in the relative proportions of products.

INTERPRETATION OF RESULTS

Decomposition of acetyl peroxide in acetic acid. The following reaction scheme for the decomposition of acetyl peroxide in acetic acid has been previously proposed (8, 10).

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[2] Graphs of the kinetic data are included in the doctoral dissertation of H. N. Friedlander, University of Chicago, 1947.

TABLE I

COMPARISON OF THE PRODUCTS OF DECOMPOSITION IN ACETIC ACID OF LEAD TETRAACETATE AND ACETYL PEROXIDE

REACTANTS	MOL. EQUIV.	MOL. EQUIV.	MOL. EQUIV.	MOL. EQUIV.	MOL. EQUIV.
Acetic acid	14	14	35	10	17
Lead tetraacetate	1	1	—	0.535	1
Acetyl peroxide	—	—	1	.465	—
Acetoxyacetic acid	—	—	—	—	1
REACTION TEMPERATURE, °C.	118	128	90	90	80
PRODUCTS	Mole/Mole $Pb(O_2CCH_3)_4$	Mole/Mole $Pb(O_2CCH_3)_4$	Mole/Mole $(CH_3CO_2)_2$	Mole/Mole $Pb(O_2CCH_3)_4$ + $(CH_3CO_2)_2$	Mole/Mole $Pb(O_2CCH_3)_4$
Lead diacetate	1.0	1.0	—	0.54	1.0
Carbon dioxide	0.42	0.31	1.52	1.24	0.46
Methane	.30	.26	1.47	0.75	.27
Methyl acetate	none	none	0.05	.03	none
Acetoxyacetic acid	0.40	0.50	none	trace	1.23[a]
Succinic acid	trace	none	0.50	0.05	trace
Methylene diacetate	0.06	0.00_1	none	.02	0.12
Formaldehyde	trace	trace	—	trace	trace
Residue	22 g.	16 g.[b]	—	7 g.	19 g.

[a] That is an increase of 0.23 mole/mole of lead tetraacetate over the initial amount.

[b] In this one case where the residue was investigated, it was found that, of the 16 grams, 9.5 grams consisted of lead salts. Undoubtedly, the other residues contained a large proportion of heavy lead salts, which accounts for their apparent large size.

TABLE II

COMPARISON OF THE PRODUCTS OF DECOMPOSITION IN ISOPROPYL ETHER OF LEAD TETRAACETATE AND ACETYL PEROXIDE

REACTANTS	MOLECULAR EQUIV.	MOLECULAR EQUIV.
Isopropyl ether	13	9
Lead tetraacetate	1	—
Acetyl peroxide	—	1
PRODUCTS	MOLE/MOLE LEAD TETRAACETATE	MOLE/MOLE ACETYL PEROXIDE
Lead diacetate	1.0	—
Carbon dioxide	0.16	0.85
Methane	.16	.76
Acetic acid	1.36	.92
Acetone	0.004	.14
Isopropyl alcohol	.005	.16
Isopropyl acetate	.01	.23
2-Isopropoxypropylene glycol diacetate	.17	—
Formaldehyde	trace	—
Residue	7 grams	21 grams

1. $(CH_3COO)_2 \xrightarrow{\Delta} CH_3\cdot + CH_3COO\cdot + CO_2$
2a. $CH_3COO\cdot \xrightarrow{\Delta} CH_3\cdot + CO_2$
2b. $2\ CH_3COO\cdot \rightarrow CH_3CO_2CH_3 + CO_2$
2c. $CH_3COO\cdot + (CH_3COO)_2 \rightarrow CH_3COOCH_3 + CH_3COO\cdot$ (and/or $CH_3\cdot + CO_2$)
3a. $CH_3\cdot + CH_3CO_2H \rightarrow CH_4 + \cdot CH_2CO_2H$
3b. $CH_3\cdot + (CH_3COO)_2 \rightarrow CH_3COO\cdot + CH_3CO_2CH_3$
3c. $CH_3\cdot + (CH_3COO)_2 \rightarrow C_2H_6 + CH_3COO\cdot + CO_2$
4. $2\ \cdot CH_2CO_2H \rightarrow (\text{—}CH_2CO_2H)_2$

Decomposition of acetyl peroxide in isopropyl ether. In the somewhat similar scheme proposed (10) for the decomposition of acetyl peroxide in isopropyl ether, reaction 1, of course, remains the same; reactions 2a, 2b, and 2c are circumvented by reaction 5b; and reactions 3b and 3c are negligible by reason of the great lability of the isopropyl ether *alpha*-hydrogen atoms, which compete for methyl (as well as acetoxy) radicals.

5a. $(CH_3)_2CHOCH(CH_3)_2 + CH_3\cdot \rightarrow CH_4 + (CH_3)_2CHO(CH_3)_2C\cdot$
5b. $(CH_3)_2CHOCH(CH_3)_2 + CH_3COO\cdot \rightarrow CH_3CO_2H + (CH_3)_2CHO(CH_3)_2C\cdot$

The formation of equal quantities of acetone and isopropyl alcohol and an amount of isopropyl acetate equal to the sum of these two products indicates, in our estimation, a common origin for these compounds. Such a community of origin might be the consequence of an acetoxy radical reaction sequence like that suggested in equations 6 and 7, competitive with the more commonly encountered hydrogen-abstraction reaction previously represented in equation 5b.

6. $CH_3COO\cdot + HC(CH_3)_2OCH(CH_3)_2 \rightarrow$ [complex] $\rightarrow CH_3COOCH(CH_3)_2 + (CH_3)_2HCO\cdot$

7. $2(CH_3)_2HCO\cdot \rightarrow CH_3COCH_3 + (CH_3)_2CHOH$

As evidence in support of the credibility of this scheme may be cited the formation of ethyl butyrate and ethyl isobutyrate when the corresponding peroxides are decomposed in the presence of ethyl ether (11).

This scheme differs somewhat from that proposed by Cass (12) for the decomposition of benzoyl peroxide in ethyl ether.

$$C_6H_5COO\cdot + CH_3CH_2OC_2H_5 \rightarrow C_6H_5COOH + CH_3(C_2H_5O)CH\cdot$$
$$CH_3(C_2H_5O)CH\cdot + (C_6H_5COO)_2 \rightarrow CH_3(C_2H_5O)CHOCOC_6H_5 + C_6H_5COO\cdot$$

However, none of the ester (equation 8) corresponding to the one obtained by Cass (12) was isolated:

8. $(CH_3)_2CHO(CH_3)_2C\cdot + (CH_3COO)_2 \rightarrow CH_3CO_2C(CH_3)_2OCH(CH_3)_2 + CH_3COO\cdot$

The probable fates of the free radicals derived from the solvent by schemes 5a and 5b is discussed later in connection with the decomposition of lead tetraacetate in isopropyl ether.

Decomposition of lead tetraacetate in acetic acid. In order to account for the low temperatures of decomposition of lead tetraacetate in many organic solvents, and for the marked solvent-dependency of lead tetraacetate decomposition rates, the assumption is made that predissociation (into free radicals) is not a prerequisite to reaction of lead tetraacetate with hydrogen donors. The available facts are more in harmony with the assumption that the first step is a bimolecular reaction between the lead tetraacetate and the solvent molecule containing an active hydrogen atom. This scheme accounts for the great differences in the reaction rates observed in the decomposition of lead tetraacetate in different solvents, and for the effects of the so-called "promoters" used by Fieser and co-workers (3, 4).

$$(CH_3COO)_4Pb + RH \rightarrow (CH_3COO)_3Pb\cdot + CH_3COOH + R\cdot$$

Acetic acid, since it contains only primary hydrogen atoms, is attacked only at elevated temperatures:

9a. $(CH_3COO)_4Pb + CH_3COOH \xrightarrow{\Delta} (CH_3COO)_3Pb\cdot + CH_3COOH + \cdot CH_2COOH$

The logical consequences of this assumption are consistent with the differences in product distribution observed in corresponding acetyl peroxide and lead tetraacetate decompositions (Tables I and II). The sequence of reactions that follows the initial bimolecular lead tetraacetate decomposition depends upon the nature of the free radicals (R·) formed from the solvent. As applied to the decomposition of lead tetraacetate in acetic acid, the following reaction scheme may be postulated:

9b. $(CH_3CO_2)_4Pb + CH_3CO_2H \rightarrow (CH_3CO_2)_3Pb\cdot + CH_3CO_2H + \cdot CH_2CO_2H$

10a. $2\ (CH_3CO_2)_3Pb\cdot \rightarrow (CH_3CO_2)_2Pb + (CH_3CO_2)_4Pb$

10b. $(CH_3CO_2)_3Pb\cdot \rightarrow (CH_3CO_2)_2Pb + CH_3COO\cdot$

10c. $(CH_3CO_2)_3Pb\cdot \rightarrow (CH_3CO_2)_2Pb + CO_2 + CH_3\cdot$

10d. $(CH_3CO_2)_3Pb\cdot + CH_3COOH \rightarrow (CH_3CO_2)_2Pb + CH_3COOH + \cdot CH_2COOH$

11. $\cdot CH_2CO_2H + (CH_3CO_2)_4Pb \rightarrow CH_3CO_2CH_2CO_2H + (CH_3CO_2)_3Pb\cdot$

12a. $CH_3COO\cdot + (CH_3CO_2)_4Pb \rightarrow (CH_3CO_2)_4Pb + CH_3COO\cdot$ (exchange)

12b. $CH_3COO\cdot + (CH_3CO_2)_3Pb\cdot \rightarrow (CH_3CO_2)_4Pb$ (recombination)

12c. $CH_3COO\cdot \rightarrow CO_2 + CH_3\cdot$

13. $CH_3CO_2CH_2CO_2H + (CH_3CO_2)_4Pb \rightarrow (CH_3CO_2)_3Pb\cdot + CH_3CO_2H + HO_2C(CH_3CO_2)CH\cdot$

14. $HO_2C(CH_3CO_2)CH\cdot + (CH_3CO_2)_4Pb \rightarrow (CH_3CO_2)_3Pb\cdot + (CH_3CO_2)_2CHCO_2H$

15. $CH_3COO\cdot + (CH_3CO_2)_4Pb \rightarrow CH_3COOCH_3 + CO_2 + (CH_3CO_2)_3Pb\cdot$

16. $CH_3\cdot + (CH_3CO_2)_4Pb \rightarrow CH_3COOCH_3 + (CH_3CO_2)_3Pb\cdot$

The initial tetraacetate-acetic acid interaction postulated (equation 9b) initiates free-radical chains. Disproportionation of the lead triacetate radical so formed (equation 10a), is, of course, a chain-terminating event and is the more common reaction at ordinary temperatures. At higher temperatures reactions 10b and 10c increase in importance and free radicals are produced. Reaction 11 takes place readily enough to circumvent reaction 4 almost completely. Acetoxy radicals,[3] incapable of attacking the solvent, either undergo the non-significant reactions 12a and 12b or decompose into carbon dioxide and methyl radicals (equation 12c). Methyl radicals react with the solvent as in the acetyl peroxide reaction (equation 3a). Acetoxyacetic acid, a better hydrogen donor than acetic acid itself, does not all survive as such but reacts further with the tetraacetate (equations 13 and 14). The methylene diacetate actually isolated is attributed to decarboxylation of diacetoxyacetic acid, which takes place readily at the temperature of the reaction.

The views here developed explain the action of lead tetraacetate in the dehydrogenation of certain hydrocarbons (*e.g.*, tetralin) and the acetoxylation of ketones and cyclic olefins as well as the "promoter" action of some compounds in methylation reactions (3, 4). [Note, however, that the oxidation of secondary alcohols and vicinal glycols (5) does not follow the scheme here outlined, but is best explained on the basis of the following series of reactions:

$$CH_3CHOHCH_3 + (CH_3CO_2)_4Pb \rightleftharpoons (CH_3CO_2)_3PbOCH(CH_3)_2 + CH_3COOH$$

$$(CH_3CO_2)_3PbOCH(CH_3)_2 \rightarrow (CH_3CO_2)_2Pb + CH_3COCH_3 + CH_3COOH$$

Here, neither methane nor carbon dioxide is formed, and the reaction proceeds at relatively low temperatures.]

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[3] The formation of methyl acetate in reactions involving acetyl peroxide and its non-formation when lead tetraacetate is used could be explained in a number of ways, none of which are, however, of a decisive nature. (a) No acetoxy radicals are formed in the reactions involving lead tetraacetate; that is, reaction 10b is of minor importance and most of the decomposition proceeds *via* 10c and 10d. (b) Reactions 15 and 16 are of minor importance. (c) Free acetoxy radicals do not disproportionate to yield methyl acetate and carbon dioxide. If this is the case then the methyl acetate formed in the reactions involving acetyl peroxide could arise as follows:

A. $CH_3CO_2\cdot \rightarrow CH_3\cdot + CO_2$
B. $CH_3\cdot + (CH_3COO)_2 \rightarrow CH_3COOCH_3 + CH_3CO_2\cdot$ (and/or $CH_3\cdot + CO_2$)
C. $CH_3CO_2\cdot + (CH_3COO)_2 \rightarrow CH_3COOCH_3 + CO_2 + CH_3\cdot$ (and/or $CH_3CO_2\cdot$)

These alternative explanations will be discussed critically in a forthcoming publication by Kharasch, J. Kuderna, and Nudenberg.

Decomposition of lead tetraacetate in isopropyl ether. It is postulated that the reaction is initiated by a solvent-tetraacetate interaction analogous to that of equation 9b (equation 17).

17. $(CH_3CO_2)_4Pb + (CH_3)_2CHOCH(CH_3)_2 \rightarrow (CH_3CO_2)_3Pb\cdot + CH_3CO_2H +$
$(CH_3)_2CHO(CH_3)_2C\cdot$

Reactions 10a, 10b, and 10c, being essentially solvent-independent, proceed as before. However, a reaction similar to 10d may here play an important role. Free methyl and free acetoxy radicals attack the solvent as in equation 18 and to a very minor extent (if at all) the lead tetraacetate as in equations 15 and 16.

18. $CH_3\cdot$ (or $CH_3COO\cdot$) $+ HC(CH_3)_2OC(CH_3)_2H \rightarrow CH_4$ (or CH_3COOH) $+$
$\cdot C(CH_3)_2OC(CH_3)_2H$

The fate of the free 2-isopropoxy-2-propyl radicals (equations 17 and 18) is more difficult to trace quantitatively. Some of them may disproportionate (equation 19),

19. $2\cdot C(CH_3)_2OCH(CH_3)_2 \rightarrow (CH_3)_2CHOC(CH_3){=}CH_2 +$
$(CH_3)_2CHOCH(CH_3)_2$

or attack lead tetraacetate to give either lead triacetate, acetic acid, and the same olefin as in 19, or react in the manner indicated in equation 20.

20. $(CH_3CO_2)_4Pb + \cdot C(CH_3)_2OCH(CH_3)_2 \rightarrow CH_3CO_2C(CH_3)_2OCH(CH_3)_2 +$
$(CH_3CO_2)_3Pb\cdot$

The non-isolation of the ester indicated as formed in equation 20 is not a weighty argument against its formation, for it might have broken down to the olefin and acetic acid, or it might have been attacked further through the secondary hydrogen atom of the isopropyl group, contributing to the "polymeric" products formed in the reaction.

A mode of reaction of 2-isopropoxy-2-propyl free radicals not previously suggested in connection with the acetyl peroxide reaction, but which might well contribute to the large amount of "polymeric" product there observed, is illustrated, in equation 19. Further reaction of the unsaturated disproportionation product with the tetraacetate (equation 21) would account for the 2-isopropoxypropylene glycol diacetate isolated.

21. $(CH_3CO_2)_4Pb + (CH_3)_2CHOC(CH_3){=}CH_2 \rightarrow (CH_3CO_2)_2Pb +$
$CH_3(CH_3CO_2)(CH_3CO_2CH_2)COCH(CH_3)_2$

EXPERIMENTAL

Reagents. Lead tetraacetate for the isopropyl ether experiments was prepared by the method described by Fieser (13) (procedure two). However, this method gave a product which contained 10% of lead chloride. This material, in the first experiments performed in acetic acid, gave methyl chloride. For that reason, in all further experiments performed in acetic acid and in the kinetic studies, the lead tetraacetate was prepared by procedure one described by Fieser (13). The lead tetraacetate was stored in a vacuum desiccator with no drying agent. It was analyzed by the following procedure. To a warm solution of lead tetraacetate in glacial acetic acid was added 10 cc. of a potassium iodide stock solution made up as follows: 150 g. of potassium iodide, 250 g. of sodium acetate (to buffer the solution), and 100 g. of sodium carbonate (to produce carbon dioxide to displace air from the flask) made up to 1 liter of solution in water. After heating the solution for one minute on a steam-bath, the liberated iodine was titrated with 0.1 N thiosulfate.[4] Lead tetraacetate prepared by procedure two was found to be 90% lead tetraacetate, whereas that from procedure one was 100% lead tetraacetate.

Isopropyl ether (Eastman practical grade) was washed three times with saturated potassium permanganate solution and distilled through a 30-plate column. Until it was used it was stored in a brown glass bottle over sodium wire.

Acetic acid was purified as described by Kharasch and Hobbs (14).

Acetoxyacetic acid was prepared from sodium acetate and chloroacetic acid and was recrystallized from benzene; m.p. 67–68°.

Methylene diacetate was prepared according to the procedure described by Knoevenagel (15); n_D^{20} 1.4048; b.p. 82° (32 mm.).

Acetyl peroxide[5] was made in 15-gram batches by the dropwise addition of 40 g. of acetic anhydride to a slurry of 46 g. of barium peroxide in 100 cc. of water and 100 cc. of ether. The temperature was kept below 10°. The ether layer was separated and dried with calcium chloride. On subsequent freezing to −80° in Dry Ice, the acetyl peroxide crystallized and was separated by decantation of the ether and removal of the last traces of solvent at low temperatures (0°) and low pressures. Analysis by the method of Kokatnur and Jelling (16) showed it to be 98% acetyl peroxide. *Care* must be taken in handling solid acetyl peroxide *for it explodes on shock.*

Reaction of lead tetraacetate with isopropyl ether. Lead tetraacetate (342 g. 0.771 mole) was placed in a 3-liter, three-necked flask fitted with a mercury-sealed stirrer and a condenser. Isopropyl ether (1021 g., 10 moles) was poured over it, and the mixture was heated to reflux with constant stirring. The evolved gases were led from the condenser through a trap immersed in a −80° bath into weighed U-tubes, the first two containing soda-lime, and the last containing Ascarite, and finally collected over water. As the reaction started, the mixture became light-yellow in color, and after a period of from eight to ten hours, the solution became colorless and gas evolution ceased.

The soda-lime and Ascarite absorption tubes had absorbed 0.125 mole of carbon dioxide. The gas collected was methane (0.124 mole; molecular weight, calculated 16.0, found 16.1). The reaction mixture was filtered to remove precipitated lead acetate, and the filtrate was distilled through a 100-plate Podbielniak HeliGrid column. An azeotropic mixture containing acetone, isopropyl alcohol, and isopropyl ether distilled first. The acetone content (0.0031 mole) was determined according to the method of Ferrante and Bloom as modified by Kharasch and Cooper (17), which employs quantitative precipitation and weighing of the 2,4-dinitrophenylhydrazone (m.p. 124.5–125°). The isopropyl alcohol (0.0035 mole) was determined by the method of Freed and Wynne (18), and the carbanilic ester (m.p. 87–87.5°) was made.

After the isopropyl ether had been removed, the higher-boiling residue was subjected to vacuum-distillation through a 10-plate column packed with concentric tubes. This separated the solution into an azeotrope of isopropyl acetate and acetic acid, pure acetic acid, and a high-boiling ester. The amount of acetic acid in the azeotrope was determined by titration. The total amount of acetic acid was 1.045 mole. The p-bromophenacyl ester was made (m.p. 124–125°). Isopropyl acetate (0.0092 mole) was determined by saponification.

Identification of the high-boiling ester. The structure of the ester, a heavy oil of light yellow color (n_D^{20} 1.4386), as 2-isopropoxypropylene glycol diacetate [$CH_3(CH_3CO_2)$

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[4] Modification of the method of Hockett and McClenahan, *J. Am. Chem. Soc.*, **61**, 1667 (1939).

[5] Modification of the method of Clover and Richmond, *Am. Chem. J.*, **29**, 179 (1903).

$(CH_3CO_2CH_2)COCH(CH_3)_2]$ was deduced from the following considerations. Derivatives of each of the fragments of the molecule following saponification were obtained. From the *hydroxyacetone* fragment was prepared a 2,4-dinitrophenylosazone which melted at 298° (corr).

Anal. Calc'd for $C_{15}H_{12}N_8O_8$: N, 25.93. Found: N, 25.22.

The compound did not depress the melting point of a known sample of the osazone (m.p. 298°) (19). From the acetic acid portion, the *p*-bromophenacyl ester was prepared (m.p. 123–125°). From the isopropyl alcohol portion, the carbanilic ester was prepared (m.p. 88–88.5° uncorr).

Anal. Calc'd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.29; Mol. wt., 218.2; Sapon. equiv., 109.1.

Found: C, 53.47; H, 7.61; Mol. wt., (cryoscopic, benzene), 217; Sapon. equiv. [Ba(OH)$_2$], 105.

The reaction of lead tetraacetate with acetic acid. In an apparatus similar to that used for the isopropyl ether runs was placed acetic acid (435 g., 7.25 moles) and lead tetraacetate (277 g., 0.512 mole). With constant stirring the solution was heated to 120°, the boiling point. As the reaction started, the mixture became light-yellow in color, and after 12 to 14 hours became dark-brown, and gas evolution ceased. The soda-lime and Ascarite absorption tubes held 9.45 g. (0.215 mole) of carbon dioxide. The gas collected was methane (0.156 mole). The clear reaction mixture was then dropped with rapid stirring into three liters of anhydrous ether, precipitating in a gummy mass the lead salts of acetic and acetoxyacetic acids. The ether solution was decanted, and the ether and acetic acid were removed by distillation through a 30-plate helix-packed column. The methylene diacetate (0.03 mole) was then distilled from the mixture at 82° (32 mm.) and checked by quantitative analysis for formaldehyde (20) produced by barium hydroxide hydrolysis. The methone derivative of formaldehyde was obtained (m.p. 189–190°, literature 189°). The remaining solids were treated with hot benzene, which extracted part of the acetoxyacetic acid (m.p. 67–68°; does not depress the melting point of an authentic sample) and a trace of succinic acid. The gummy mass of lead salts was dissolved in glacial acetic acid, and the lead was precipitated as lead chloride by dry gaseous hydrogen chloride. The filtered acetic acid solution was subjected to distillation, which removed the acetic acid and left a residue which when treated with hot benzene yielded the remainder of the acetoxyacetic acid, giving a total of 0.202 mole. The acetoxyacetic acid was further identified by conversion to the amide of glycolic acid (m.p. 116–117°, literature 118.5–119.5°).

The reaction of lead tetraacetate and acetyl peroxide with acetic acid. For this reaction the following modification of the above procedure was used. The acetyl peroxide, dissolved in acetic acid, was added dropwise below the surface of a solution of lead tetraacetate in acetic acid held at 90°. For quantitative data see Table I, column 5. The succinic acid obtained melted at 184–186° (literature 186–188°), and did not depress the melting point of an authentic sample.

The rate of reaction of lead tetraacetate with acetic acid. The kinetic studies were run in a cylindrical vessel about 20 cm. long and 6 cm. in diameter fitted with a Trubore stirrer, a capillary tube leading below the liquid level, and a condenser leading to a eudiometer.

The appropriate solutions were placed in the vessel, and the lead tetraacetate was added. The solution was then rapidly heated to the reflux point (120°) in an oil-bath whose temperature was carefully controlled.

The samples for titration were withdrawn from the capillary and weighed into tared flasks, then analyzed in the same manner as samples of pure lead tetraacetate (see section, "Reagents"). The rate of gas evolution, as measured in the eudiometer, roughly paralleled the rate of decomposition of the lead tetraacetate.

SUMMARY

Reaction schemes for the reactions of lead tetraacetate with isopropyl ether and acetic acid have been postulated. The schemes proposed involve bimolecular

oxidations of the solvents by the lead tetraacetate, producing free lead triacetate radicals and solvent free radicals. The free lead triacetate radicals can either disproportionate or decompose to give free acetoxy radicals or free methyl radicals and carbon dioxide. The solvent free radicals can either disproportionate, dimerize, or react with lead tetraacetate.

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