

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF LIVERPOOL, ENGLAND]

## The Decomposition of Plumbic Acetate in Anhydrous Acetic Acid

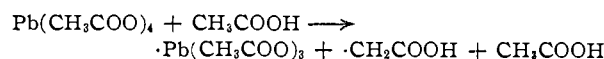
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The kinetics of the decomposition of plumbic acetate in anhydrous acetic acid containing sodium acetate have been investigated. No evolution of carbon dioxide or methane accompanied the decomposition under these conditions. The reaction was found to be of a complex nature, the rate of decomposition decreasing with the increase in initial plumbic acetate concentration. Retardation by reaction products is suggested as an explanation of this behavior and on this assumption a reaction scheme is proposed which gives a rate expression fitting the experimental kinetic data. An ionic plumbic acetate species is necessary to the kinetic scheme and the identification of this species is discussed.

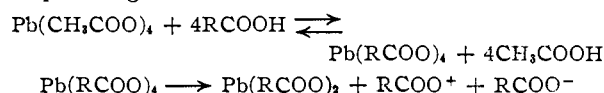
## Introduction

No kinetic data have been published for the decomposition of plumbic acetate, but Kharasch, Friedlander and Urry<sup>1</sup> have mentioned that the kinetics obtained from their study of the decomposition are complicated. They carried out the decomposition in acetic acid at reflux temperatures and measured the evolution of carbon dioxide and methane. From the identification of reaction products they were able to formulate a mechanism for the decomposition, giving as the first step in their mechanism



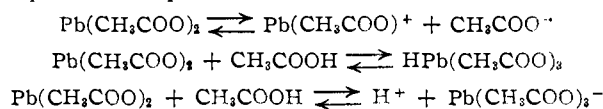
Since the products of this decomposition differed from those obtained from the decomposition of acetyl peroxide, it was assumed that the plumbic acetate does not decompose to give acetoxy radicals but the  $\cdot\text{CH}_2\text{COOH}$  radical. By suitable reactions involving the two radicals produced in the initial step the identified reaction products could be accounted for.

Mosher and Kehr<sup>2</sup> investigated the decomposition of certain organic acids in the presence of plumbic acetate, but again no kinetics were given and the mechanism of reaction was based on identified products. The mechanism proposed by these workers is opposed to that of Kharasch and co-workers<sup>1</sup> in that it is ionic in nature, the initial steps being



The essential similarity between these two schemes, however, lies in the fact that the decomposition involves both the plumbic acetate and the solvent in the primary reaction step in each case.

Evans, Huston and Norris<sup>3</sup> investigated the isotopic exchange between both plumbous and plumbic acetate and acetic acid solvent, using <sup>14</sup>C-labeled acetate groups. Rapid exchange was observed, and it was suggested that one or more of three equilibria for plumbous acetate existed



(1) M. S. Kharasch, H. N. Friedlander and W. H. Urry, *J. Org. Chem.*, **16**, 533 (1951).

(2) W. A. Mosher and C. L. Kehr, *THIS JOURNAL*, **75**, 3172 (1953).

(3) E. A. Evans, J. L. Huston and T. N. Norris, *ibid.*, **74**, 4985 (1952).

A similar set of equilibria was postulated for plumbic acetate. Burns and Hume<sup>4</sup> examined the species of plumbous acetate formed in aqueous solution containing sodium acetate and concluded that several ionic species exist, including a  $\text{Pb}(\text{CH}_3\text{COO})_3^-$  ion.

Work in this Laboratory on the oxidation of metal acetates by plumbic acetate in anhydrous acetic acid<sup>5</sup> has indicated that ionic species of both reactants take part in these reactions. It was also noticed that though plumbic acetate is stable in the pure solvent, a marked decomposition occurs in the presence of sodium acetate, even at room temperature. The present investigation thus was undertaken to study the decomposition of the lead salt under conditions suitable for accurate kinetic measurement and to obtain information on the formation of ionic plumbic acetate species.

## Experimental

**Materials.** Plumbic acetate: Prepared by the method of Dimroth and Schweizer,<sup>6</sup> recrystallized from acetic acid, pumped dry and stored under a vacuum. Purity, estimated by iodometric titration, was determined as 100%.

Sodium acetate: "Analar" reagent quality, recrystallized from acetic acid and pumped under a vacuum for 10 hr. at 120°.

Glacial acetic acid: "Analar" reagent, purified by refluxing with chromium trioxide and acetic anhydride followed by distillation. All other reagents were of "Analar" quality, recrystallized from acetic acid, where possible, and pumped for 10 hr. at 120° under a vacuum to remove all trace of water.

**Technique and Apparatus.**—Kinetic measurements were carried out over a temperature range 50 to 80°, the disappearance of the plumbic salt being followed by using a spectrophotometric technique. A 10-ml. solution of plumbic acetate and a 10-ml. solution of sodium acetate, thermostated at the required reaction temperature, were mixed; at known time intervals, 1-ml. aliquots of the reactant solution were pipetted into 10 ml. of acetic acid and the optical density of the resulting solution measured at 300 m $\mu$ ; all measurements were made on an S.P. 500 Unicam Spectrophotometer. The absorption spectra of plumbic and plumbous acetates are shown in Fig. 1. None of the reaction products had any appreciable absorption at the wave length used for following the kinetic study. Further kinetic data were obtained by estimating the plumbic acetate concentration by iodometric titration. The two methods gave concordant results showing that the measured optical densities are proportional to the unreacted plumbic acetate concentration.

Experiments to detect gas evolution from reactant solutions of molarities used in the kinetic study were performed. An extremely sensitive differential manometer was used, a solution of the lead salt in acetic acid containing sodium acetate being compared to a solution of sodium acetate of the same molarity. The two solutions were connected *via* the manometer and agitated at 10 c.p.s. while immersed in a wa-

(4) E. A. Burns and D. N. Hume, *ibid.*, **78**, 3958 (1956).

(5) L. H. Sutcliffe and J. Walkley, *Nature*, **178**, 999 (1956).

(6) O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

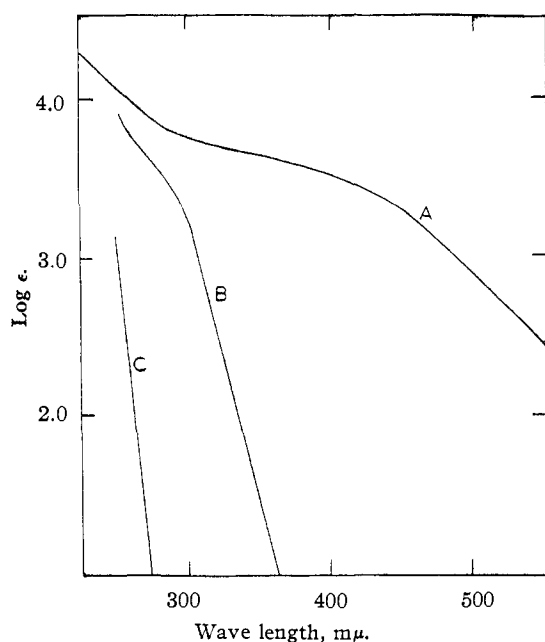
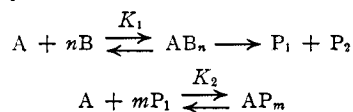


Fig. 1.—The absorption spectra of: A, plumbic acetate in ethyl alcohol; B, plumbic acetate in acetic acid; C, plumbous acetate in acetic acid.

ter thermostat. No production of gas accompanied the decomposition as carried out under these conditions.

In order to identify reaction products the decomposition was carried out in a closed system, both in the presence and in the absence of sodium acetate. The latter conditions repeated the work of Kharasch and co-workers,<sup>1</sup> the gases evolved being trapped and later identified by chromatographic analysis as carbon dioxide and methane. In the presence of sodium acetate no gases were evolved even when reflux conditions were used. The products of the decomposition in the presence of sodium acetate were identified by the technique described by Kharasch.<sup>1</sup> Acetoxyacetic acid was isolated, recrystallized from benzene and identified by infrared analysis. The possible presence of other aliphatic acids was investigated by a paper chromatographic method<sup>7</sup> on the ether extract following the complete precipitation of the lead as lead chloride by passing dry hydrogen chloride gas into the reaction mixture. A trace of glycolic acid was identified and it was also clear that another aliphatic acid was present, presumably acetoxyacetic acid. A small amount of succinic acid was detected using microspot techniques.

**Kinetic Measurements.**—Using a constant molarity of sodium acetate (1.0 *M*) it was observed that the rate of decomposition decreased with the increase in the initial plumbic acetate molarity. Further experiments, in which product solution from a completed decomposition was added to a new reactant solution, showed that the subsequent reduction in rate and extent of reaction could be attributed to a product species. This is illustrated in Fig. 2. Such behavior and the dependence of rate on initial concentration is typical of a reaction in which retardation occurs through some equilibrium step involving a product species and the decomposing molecule. The simplest type of reaction scheme involving such a dependence would be



In this instance  $[A] = [\text{Pb}(\text{OAc})_4]$ ,  $[B] = [\text{OAc}^-]$ , and  $[P_1]$  some product species. From the expression for the two proposed equilibria, substitution into the rate expression

$$-\frac{d[\text{Pb}(\text{IV})]}{dt} = k_2[\text{Pb}(\text{CH}_3\text{COO})_n^{2-}]$$

(7) F. W. Denison and E. F. Phares, *Anal. Chem.*, **24**, 1628 (1952).

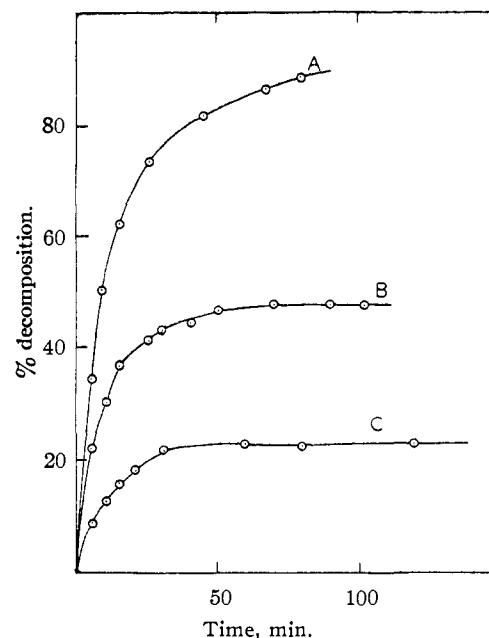


Fig. 2.—The effect of added product solution on decomposition rate: temp.  $70.1 \pm 0.01^\circ$ ; sodium acetate 1.0 *M*; A, no product added; B, product solution added from decomposition of  $4.8 \times 10^{-4}$  *M* Pb(IV); C product solution added from decomposition of  $9.5 \times 10^{-4}$  *M* Pb(IV).

gives a rate law

$$-\frac{d[\text{Pb}(\text{IV})]}{dt} = \frac{k_2[A][B]^n}{[B]^n + K_1 + \frac{K_1}{K_2}([A]_0 - [A])}$$

The integration of this expression gives

$$\left(1 + \frac{K_1}{[B]^n} + \frac{[A]_0 K_1}{K_2 [B]^n}\right) \ln \frac{[A]_0}{[A]} - \frac{([A]_0 - [A])}{K_2 [B]^n} \times K_1 = k_2 t$$

A further discussion and more rigorous derivation of the rate law will be given later in the paper, but simplification of this expression and substitution of optical density units gives

$$\frac{2.303 D_0}{l} \log \frac{D_0}{D_t} - \frac{D_0 - (D_t)}{l} = C t$$

*C* being an arbitrary constant involving  $K_1$ ,  $K_2$ , etc.  $D_0$  is optical density at time  $t = 0$ ;  $l$  = cell length  $\epsilon$  is extinction coefficient of Pb(IV)

Figure 3 shows the experimental data plotted to the above expression, plots for different initial plumbic acetate concentrations having a common intercept, and the slopes of the plots are proportional to  $D_0$ . Table I provides the intercept and (slope)/ $D_0$  values taken from Fig. 3. The fact that the latter values are somewhat greater than 2.303 is a consequence of the drastic simplification of the equation with regard to the pre-log  $D_0/D_t$  term.

TABLE I

| Initial concn., <i>M</i> | Slope | Slope/ $D_0$ | Intercept, min <sup>-1</sup> |
|--------------------------|-------|--------------|------------------------------|
| $4.0 \times 10^{-4}$     | 13.5  | 2.60         | -0.0024                      |
| $10 \times 10^{-4}$      | 3.64  | 2.66         | -0.0041                      |
| $7.5 \times 10^{-4}$     | 2.10  | 2.54         | -0.0021                      |
| $6.25 \times 10^{-4}$    | 1.78  | 2.58         | -0.0025                      |
| $5.0 \times 10^{-4}$     | 1.45  | 2.46         | -0.0025                      |

The addition of product solution, as seen in Fig. 2, justifies the retardation by product assumption, but the addition to the reactant solution of identified reaction products and of other possible products, as given in Table II, failed to bring about any retardation. A tenfold excess of lead diacetate, or water, again failed to retard the reaction, the retarding species could not, therefore, be identified.

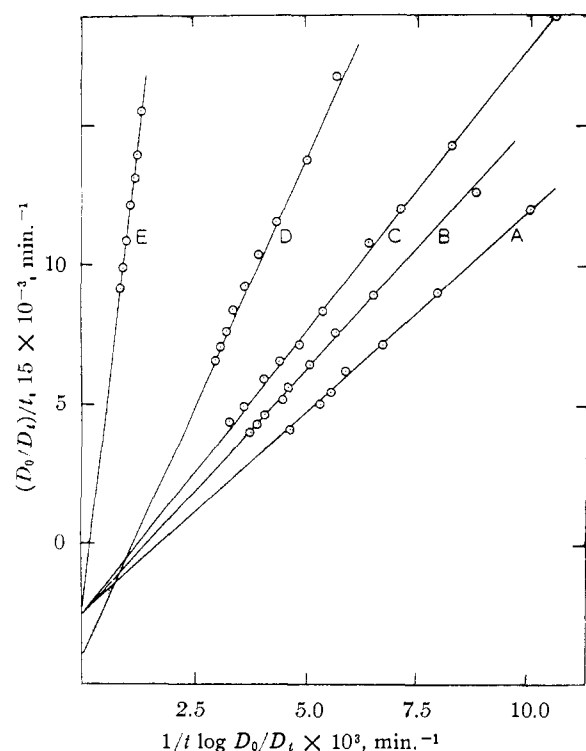


Fig. 3.—Rate law for disappearance of Pb(IV) at 70.1  $\pm$  0.01 $^\circ$ ; sodium acetate 1.0  $M$ ; initial Pb(IV) concentration: A,  $5.0 \times 10^{-4} M$ ; B  $6.25 \times 10^{-4} M$ ; C,  $7.50 \times 10^{-4} M$ ; D,  $10.0 \times 10^{-4} M$ ; E,  $40.0 \times 10^{-4} M$ .

For the identification of reaction products it was necessary to use a solution of plumbic acetate of high molarity. For a typical experiment ( $[Pb(IV)] = 0.5 M$ ;  $[NaOAc] = 1.0 M$ ) carried out at 70 $^\circ$ , after approximately 25% decomposition had occurred the concentration of Pb(IV) remained constant. The reaction could only be brought to completion by refluxing the solution.

TABLE II

EFFECT OF ADDITION OF POSSIBLE DECOMPOSITION PRODUCTS ON THE RATE OF DECOMPOSITION

All additions were of molarity  $2.0 \times 10^{-2} M$ , temperature 70.0 $^\circ$

| Addition of        | Effect on Rate |
|--------------------|----------------|
| Acetoxyacetic acid | No effect      |
| Succinic acid      | No effect      |
| Glycolic acid      | Acceleration   |
| Methyl acetate     | No effect      |
| Ethyl acetoacetate | No effect      |
| Acetyl peroxide    | Acceleration   |
| Plumbous acetate   | No effect      |
| Water              | No effect      |

**Radical Production during Decomposition.**—An attempt to determine the possible production of radicals during the decomposition was made by initiating the polymerization of suitable monomers, for example, methyl methacrylate, styrene and acrylonitrile, followed by end group analysis and identification by infrared spectroscopy. In the presence of the monomer, however, a new mechanism became operative, the monomer being oxidized directly at 20.0 $^\circ$  by the plumbic salt, leading to polymer production. The decomposition was also studied in the presence of the stable free radical  $\alpha, \alpha'$ -diphenyl- $\beta$ -picrylhydrazyl. The kinetics of the decomposition should have been modified by the prevention of retarder formation, but direct electron transfer to the free radical from the plumbic salt occurred.<sup>8</sup> The rate

(8) L. H. Sutcliffe and J. Walkley, to be published.

of this oxidation was much faster than the rate of decomposition of the plumbic salt.

**Effect of Sodium Acetate.**—The dependence of the reaction rate on the sodium acetate concentration was determined from the value of the intercept obtained from experimental plots typified by Fig. 3. The data are shown in Table III, the constancy of intercept/(NaOAc) at any

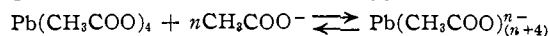
TABLE III

| Temp., $^\circ C.$ | (NaOAc), $M$ | Intercept (min. $^{-1}$ ) | Intercept (NaOAc), $M^{-1}$ , min. $^{-1}$ |
|--------------------|--------------|---------------------------|--|
| 74.8               | 1.00         | 0.0033                    | 0.0033                                     |
| 74.8               | 0.75         | .0022                     | .0029                                      |
| 74.8               | 0.50         | .0014                     | .0028                                      |
| 70.0               | 1.00         | .0014                     | .0014                                      |
| 70.0               | 0.50         | .0012                     | .0015                                      |
| 70.0               | 0.60         | .0008                     | .0013                                      |
| 65.0               | 1.00         | .0013                     | .0013                                      |
| 65.0               | 0.75         | .0008                     | .0011                                      |
| 65.0               | 0.50         | .0005                     | .0010                                      |
| 55.0               | 1.00         | .0006                     | .0006                                      |
| 55.0               | 0.75         | .0004                     | .0005                                      |

temperature indicating the decomposition has a second-order dependency on the acetate ion concentration. This assumes  $[OAc^-] = K^{1/2}[NaOAc]^{1/2}$ , which is justified since the dissociation constant of sodium acetate in acetic acid at 25 $^\circ$  is only  $2.08 \times 10^{-7}$  and both plumbous and plumbic acetate are much weaker electrolytes than sodium acetate. The most likely explanation of this acetate ion dependence is that one or more complex ions of  $Pb(CH_3COO)_4$  is taking part in the reaction and ion migration experiments were performed to provide an indication of the charge carried by these species. In the pure acetic acid a potential of 500 volts showed slight migration to both anode and cathode, but in the presence of sodium acetate the migration was mainly toward the anode and to a much greater extent. A spectrophotometric investigation of plumbic acetate was made in the temperature range 20 to 30 $^\circ$  by measuring optical densities at 270, 300 and 330  $m\mu$ . The value of the observed extinction coefficient for plumbic acetate in the pure solvent was found to vary slightly with temperature, which suggests that a solvation equilibrium of the type



may have been disturbed. Such an equilibrium may well account for the remarkable stability of plumbic acetate in acetic acid compared to other solvents. The possibility that this species might dissociate to give hydrogen ions was investigated by the effect of the addition of perchloric and trichloroacetic acids, but no change in absorption was observed. The addition of sodium acetate at concentrations up to 1.0  $M$  brought about slight increases in the observed extinction coefficient, but these changes in absorption were too small to allow quantitative data to be obtained. In view of the lack of any  $[H^+]$  dependence and the indication from ion migration experiments that an increased concentration of a negative Pb(IV) ion is formed in the presence of sodium acetate it would seem that the important equilibria (omitting solvation molecules) will be of the type



the acetate ion dependence of the decomposition suggesting that  $n = 2$ .

### Discussion

The effect of increased initial concentration bringing about a decrease in the reaction rate has been observed by Levy and Szwarc<sup>9</sup> for the decomposition of acetyl peroxide in acetic acid and also by Stannett and Mesrobian<sup>10</sup> in their study of the decomposition of cumene hydroperoxide in benzyl alcohol. No explanation of these effects was given

(9) M. Levy and M. Szwarc, *THIS JOURNAL*, **76**, 5981 (1954).

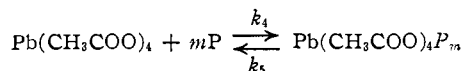
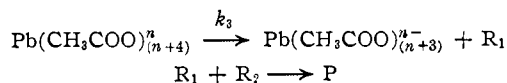
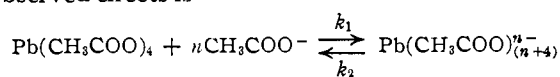
(10) V. Stannett and R. B. Mesrobian, *ibid.*, **72**, 4125 (1950).

in terms of a rate law, but it was suggested that the effect was due to hydrogen bonding, ionic factors or to retardation by reaction products.

In the present study the kinetic expression found to express the observed rate data implies the retardation is brought about by the formation of a product. The plumbic acetate may be regarded as forming a relatively stable complex with this "retarder" which may only be broken down under the more rigorous conditions of refluxing. The rate law used to eliminate the dependence on initial concentration is an integrated form of the expression

$$\frac{dx}{dt} = \frac{k(a-x)}{b+cx}$$

the expression being general to kinetic schemes involving an initial concentration dependence. The use of the integrated law allowed an over-all activation energy for the decomposition of  $16 \pm 4$  kcal./°C./mole to be evaluated and indicated a second-order dependence on the acetate ion. The most plausible mechanism incorporating all the observed effects is



where  $\text{R}_1$  and  $\text{R}_2$  are probably radicals and  $\text{P}$  the reaction product bringing about the observed retardation. From the expressions for the two proposed equilibria, substitution into the rate expression

$$\frac{-d[\text{Pb(IV)}]}{dt} = k_3 [\text{Pb}(\text{CH}_3\text{COO})_{(n+4)}^-]$$

gives a rate law of the type required. The only assumption necessary is that  $m = 1$  and that most of the  $\text{Pb(IV)}$  exists in the uncomplexed form. A more fundamental treatment of the above reaction scheme is to assume a steady state to exist for the the concentration of the anionic  $\text{Pb}(\text{CH}_3\text{COO})_{(n+4)}^-$  species, and this gives rise to a kinetic expression

$$\frac{-d[\text{Pb(IV)}]}{dt} = \frac{k_3[\text{Pb(IV)}]_t \times [\text{OAc}^-]^n}{[\text{OAc}^-]^n + \left(\frac{k_2+k_3}{k_1}\right) + \left(\frac{k_2+k_3}{k_1}\right) [\text{P}]} \quad (1)$$

using for convenience the notation  $[\text{OAc}^-]$  for acetate ion concentration, and  $[\text{Pb(IV)}]_t$  the plumbic acetate concentration at any time "t." The concentration of the "retarder"  $\text{P}$  is given by

$$[\text{Pb(IV)}]_0 - [\text{Pb(IV)}]_t = [\text{Pb(OAc)}_4\text{P}] + [\text{P}]$$

and thus

$$\frac{-d[\text{Pb(IV)}]}{dt} = \frac{k_3[\text{Pb(IV)}]_t [\text{OAc}^-]^n}{A + \left(\frac{k_4}{k_5}\right) \left(\frac{k_2+k_3}{k_1}\right) \{ [\text{Pb(IV)}]_0 - [\text{Pb(IV)}]_t \}} \quad (2)$$

if it is assumed that the magnitude of  $[\text{OAc}^-]^n$  and the terms involving  $[\text{Pb(OAc)}_4\text{P}]$  are small com-

pared to the term involving  $[\text{Pb(IV)}]_0 - [\text{Pb(IV)}]_t$ . This is the equation used to express the experimental data. Equation 1 may be simplified in another manner, using the relationship

$$\left(\frac{k_4}{k_5}\right) [\text{P}] = \frac{[\text{Pb(OAc)}_4\text{P}]}{[\text{Pb(OAc)}_4]}$$

and assuming that most of the plumbic salt exists in the uncomplexed form, that is, from the mass balance

$$[\text{Pb(IV)}]_t = [\text{Pb(OAc)}_4] + [\text{Pb(OAc)}_{(n+4)}^-] + [\text{Pb(OAc)}_4\text{P}]$$

that  $[\text{Pb(IV)}]_t = [\text{Pb(OAc)}_4]$ . The rate equation now becomes

$$\frac{-d[\text{Pb(IV)}]}{dt} = \frac{k_3[\text{Pb(IV)}]_t^n [\text{OAc}^-]^n}{[\text{Pb(IV)}]_t [\text{OAc}^-]^n + \left(\frac{k_2+k_3}{k_1}\right) \{ [\text{Pb(IV)}]_t + [\text{Pb(OAc)}_4\text{P}] \}}$$

Since  $[\text{Pb(IV)}]_0 - [\text{Pb(IV)}]_t = [\text{Pb(OAc)}_4\text{P}] + [\text{P}]$  and assuming

$$\frac{k_1+k_3}{k_2} [\text{Pb(IV)}]_0 \gg [\text{Pb(IV)}]_t [\text{OAc}^-]$$

then the rate expression reduces to

$$\frac{-d[\text{Pb(IV)}]}{dt} = \frac{k_3[\text{Pb(IV)}]_t^n [\text{OAc}^-]^n}{\left(\frac{k_2+k_3}{k_1}\right) [\text{Pb(IV)}]_0 - \left(\frac{k_2+k_3}{k_1}\right) [\text{P}]}$$

The derivation of this form of the kinetic expression would suggest that the kinetic data may be plotted as second order in  $[\text{Pb(IV)}]$ . Figure 4 illustrates such a plot for the same data used in Fig. 3, a good second-order obeyance is observed

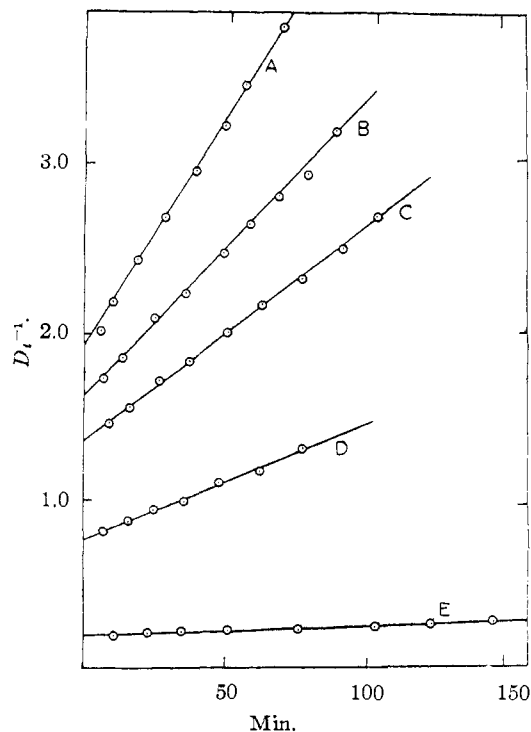


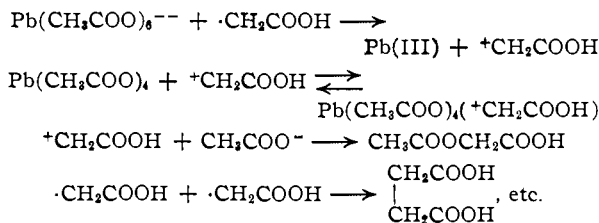
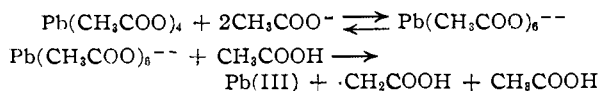
Fig. 4.—Apparent second-order nature of the  $\text{Pb(IV)}$  decomposition; temp.  $70.1 \pm 0.01^\circ$ ; sodium acetate  $1.0 M$ ; plumbic acetate: A,  $5.0 \times 10^{-4} M$ ; B,  $6.25 \times 10^{-4} M$ ; C,  $7.50 \times 10^{-4} M$ ; D,  $10.0 \times 10^{-4} M$ ; E,  $40.0 \times 10^{-4} M$ .

and an obvious dependence on the initial [Pb(IV)] concentration can be seen. It must be emphasized that this pseudo second-order relationship arises purely from the treatment of the kinetic scheme and in no way indicates any necessity for having two plumbic acetate molecules in the rate-determining step.

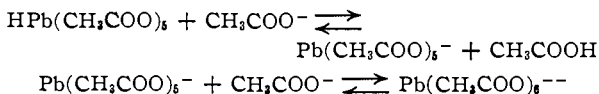
The lack of any correlation between the second-order rate constant and the [Pb(IV)]<sub>0</sub> molarity suggests that the term  $\frac{[k_2+k_3]}{k_1} [P]$  cannot be ignored.

The magnitude for [P] agrees with the requirement in the first derivation that [Pb(OAc)<sub>4</sub>P] should be small. This implies that the retardation equilibrium be in the direction of non-complexing, or since in the mass balance the only product considered was "P," this may suggest that the amount of P being used in other reactions is large compared to the amount required for forming the retarding complex. The inclusion of other non-rate determining steps in the proposed reaction mechanism does not affect the form of the rate equation derived in the above manner. It is of interest, however, that no rate law of the type necessary to express the kinetic data can be obtained if the retardation equilibrium is assumed to involve the anionic Pb(CH<sub>3</sub>COO)<sub>n+4</sub><sup>-</sup> species.

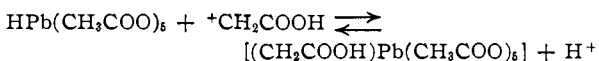
The dependence of the reaction rate on the acetate ion concentration is a most important feature of the present study since it suggests that the most reactive species of plumbic acetate is one containing two acetate ions. In formulating the rate laws it was necessary to assume that these anionic complexes are present in only very low concentration, which is in agreement with the small spectrometric changes found in the study of the Pb-(CH<sub>3</sub>COO)<sub>4</sub>-(CH<sub>3</sub>COO<sup>-</sup>) system. The retarder "P" could not be identified as any of the observed reaction products, thus suggesting that it is probably an intermediate product. The authors propose that the ion <sup>+</sup>CH<sub>2</sub>COOH is the species acting as the retarder. The precise identity of this ion cannot be determined experimentally, but it is in agreement with the decomposition schemes of both Kharasch and co-workers<sup>1</sup> and Mosher and Kehr.<sup>2</sup> It can be seen that this ion may be produced either by direct decomposition of the plumbic ion species or in the production of the  $\cdot$ CH<sub>2</sub>COOH radical and subsequent oxidation. The <sup>+</sup>CH<sub>2</sub>COOH ion then forms a relatively stable complex with the lead salt. The simplest reaction mechanism is



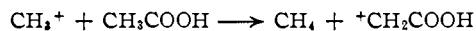
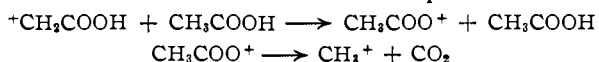
All solvation has been ignored in the above scheme but consideration of the production of the acetate anionic Pb(IV) species, and the retarder complex, suggests that these equilibria would be best written



The interpretation of the retardation equilibrium now becomes



this complexed neutral species no longer entering into any equilibria with acetate ions. The lack of evolution of methane and carbon dioxide in this study may be considered as due to the presence of the acetate ion, available for the direct formation of acetoxyacetic acid rather than the attack of the <sup>+</sup>CH<sub>2</sub>COOH ion on the solvent which would occur if the acetate ion were not present. This



will account for the gas evolution reported in previous studies. From the color change of the solution during the decomposition as carried out under the conditions employed by Kharasch and co-workers,<sup>1</sup> it would appear that with the production of the lead dioxide that a heterogeneous mechanism is superimposed on the normal decomposition.

The <sup>+</sup>CH<sub>2</sub>COOH ion was proposed by Mosher and Kehr,<sup>2</sup> though in their reaction scheme it was formed as a secondary reaction product from an attack on the solvent by the CH<sub>3</sub>COO<sup>+</sup> ion. The stability of this ion was suggested by these authors to arise from the interaction of the positive charge with the electrons of the carbonyl group, giving a resonance type stabilization.

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