

to both enzyme-catalyzed hydration of CH_3CHO and dehydration of $\text{CH}_3\text{CH}(\text{OH})_2$.

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The Mechanism of Oxidative Decarboxylation with Lead(IV) Acetate

Sir:

Recently there has been increased discussion¹ concerning the mechanism of lead tetraacetate oxidation² of organic compounds, particularly oxygenated species. The conversion of Pb(IV) to Pb(II) has often been postulated to involve a direct 2-equiv. transformation with

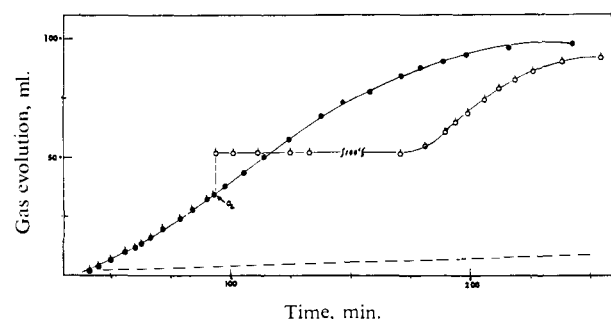


Figure 1. Decomposition of valeric acid with 0.2 M lead(IV) acetate in benzene at 81° (-----). Catalysis by pyridine (●). Inhibition by oxygen (○).

concomitant formation of carbonium ion or cationic intermediates. The case for the participation of free radicals has been made, although definitive studies are lacking.³ We wish to present evidence that the *oxidative decarboxylation of carboxylic acids with lead(IV) acetate proceeds via a free radical chain process.*

The decarboxylation of aliphatic acids⁴ is generally slow in refluxing benzene, but is catalyzed by pyridine.⁵ Under both conditions, *n*-valeric acid is decomposed at 81° to butane, butene-1, carbon dioxide, *n*-butylbenzene, *sec*-butyl acetate, and valerate. The onset of reaction is characterized by an induction period which is drastically shortened by degassing. The rate of gas evolution in the presence of pyridine follows a typical

(1) For leading recent references see: W. H. Starnes, Jr., *J. Am. Chem. Soc.*, **86**, 5603 (1964); S. Moon and J. M. Lodge, *J. Org. Chem.*, **29**, 3453 (1964); D. Hauser, K. Kalvoda, H. Heusler, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1883, 1961 (1964).

(2) R. Criegee, *Angew. Chem.*, **70**, 173 (1958).

(3) Nuclear methylation and phenylation of aromatic compounds with lead(IV) acetate and benzoate have been noted (L. F. Fieser, *et al.*, *J. Am. Chem. Soc.*, **64**, 2043, 2052 (1942); D. H. Hey, *et al.*, *J. Chem. Soc.*, 2747 (1954); 3963 (1955); D. I. Davies, *ibid.*, 2351 (1963)]. However their significance with respect to oxidative decarboxylations in general^{1,2,4} has not been delineated.

(4) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953); D. Benson, L. Sutcliffe, and J. Walkley, *ibid.*, **81**, 4488 (1959); E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963).

(5) C. A. Grob, M. Ohta, and A. Weiss, *Angew. Chem.*, **70**, 343 (1958).

sigmoid curve as shown in Figure 1. If oxygen is introduced at an intermediate point, the reaction stops abruptly and resumes spontaneously after an inhibition period (proportional to the oxygen present) or sooner, if oxygen is removed by flushing.

The decarboxylation also proceeds readily at 81° in the absence of pyridine if a catalytic amount of cupric salt is added and the oxygen scrupulously removed (Figure 2). The rapid decarboxylation under these conditions can be instantaneously interrupted with oxygen, and remains completely inhibited for prolonged (and indefinite) periods of time and not until the oxygen is removed, at which time it continues in a manner previous to its inhibition (Figure 2).

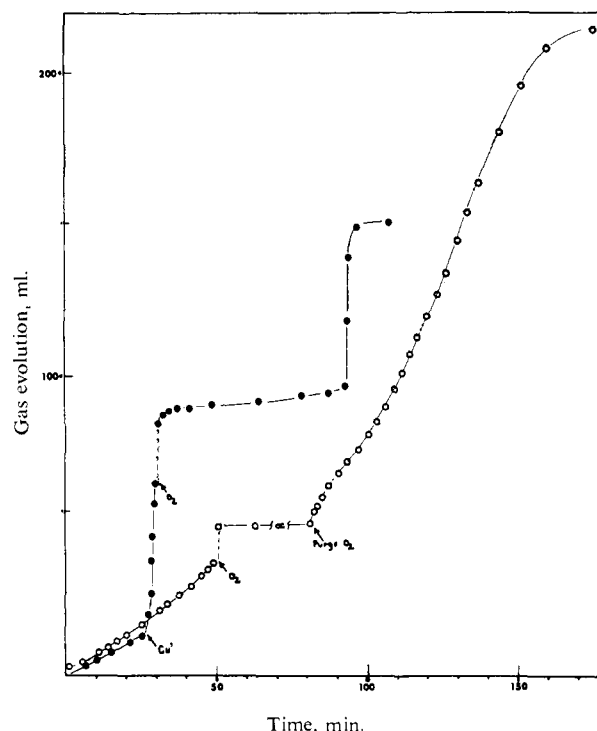
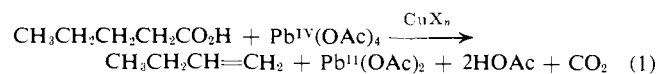


Figure 2. Decomposition of valeric acid with 0.2 M lead(IV) acetate catalyzed by copper salts. O, No pyridine, 0.045 M copper(II) acetate, inhibition by oxygen. ●, With pyridine, catalysis by 3.7×10^{-4} M copper(I) acetate, inhibited by oxygen.

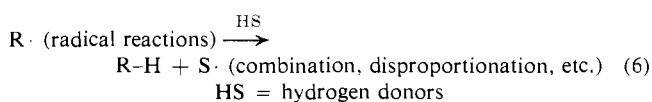
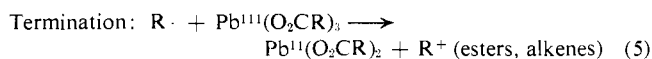
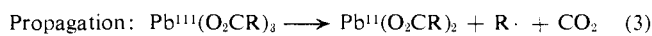
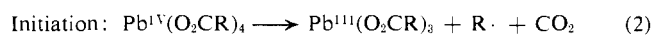
The rate of decarboxylation of valeric acid by Pb(IV) in the presence of pyridine is additionally catalyzed in a remarkable manner by copper acetate as shown in Figure 2. However rapid this reaction is, it is strongly inhibited by oxygen (Figure 2), and remains quiescent until the added oxygen is consumed, and then resumes abruptly. The products of decomposition in the presence of copper salts are independent of the pyridine and the stoichiometry is given by eq. 1. No significant amounts of esters or butylbenzenes are formed under these conditions. A similar behavior is shown by iso-



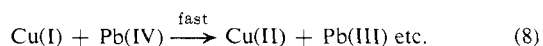
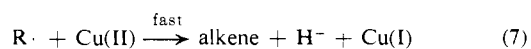
valeric and 2-methylbutyric acids. The latter, being secondary, is less sensitive to oxygen effects and the length of inhibition (not retardation) is shorter. Moreover, the copper-catalyzed decarboxylation of the

secondary acid, after inhibition by oxygen, will reinitiate itself after several hours.

The marked and reversible inhibition by oxygen, the catalysis by copper salts and valeryl peroxide, and the nature of the products of decomposition are strong support for a mechanism which involves a free radical chain process, and *lead(III) is implicated as an intermediate*.⁶ The following sequence is proposed



Such a mechanism can readily account for the catalysis by copper salts. Alkyl radicals are known to be scavenged effectively by Cu(II) to form alkenes (eq. 7).⁸ Cu(I) is subsequently reoxidized (eq. 8) by Pb(IV)



to regenerate Cu(II) and the metastable Pb(III) intermediate. The latter reaction is also rapid since lead(IV) carboxylates are instantaneously reduced by Cu(I) at room temperature. In this manner the slower oxidation of alkyl radicals by Pb(IV) in the propagation step (4) is circumvented and alkenes characteristic of Cu(II) oxidations⁵ are major products. The butyl radical from valeric acid also can be trapped⁹ with butadiene to yield a mixture of 1-acetoxyoctene-2 and 3-acetoxyoctene-1, and *sec*-butyl radical from 2-methylbutyric acid can also be diverted with oxygen to afford a mixture of methyl ethyl ketone and *sec*-butyl alcohol.

The key reactions in the proposed chain process are the propagation steps (3) and (4). The spontaneous dissociation (3) of the metastable Pb(III) intermediate is similar to that postulated for the fragmentation of triethyllead(III) during reduction of triethyllead(IV).¹⁰ The rates of oxidation (4) of alkyl radicals by Pb(IV) are dependent on the structure of R in accord with their ionization potentials.¹¹ Thus, secondary and tertiary radicals are largely oxidized to esters, alkenes, and products derived from carbonium ion intermediates. 2-Methylbutyric acid forms *sec*-butyl acetate (25%) and 2-methylbutyrate (35%) in good yield, together with a mixture of butene-1 (7%), *cis*- (4%) and *trans*- (8%) butene-2, *n*-butane (9%), and *sec*-butylbenzene (10%). In contrast, the primary isovaleric and valeric acids give mainly products such

(6) Studies to identify Pb(III) intermediates are in progress. Other mechanisms without Pb(III) can be considered at the sacrifice of simplicity.

(7) R⁺ denotes formal oxidation state only. Equations balanced as esters (R'O₂CR) or alkenes (C₂H₄ + HO₂CR), etc.

(8) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963); H. E. DeLaMare, J. K. Kochi, and F. F. Rust, *ibid.*, **85**, 1437 (1963).

(9) J. K. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, in press.

(10) C.-H. Wang, P. L. Levins, and H. G. Parris, *Tetrahedron Letters*, 687 (1964).

(11) From the gas phase, R. Taubert and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 1525 (1962).

as isobutane (30–40%) and *n*-butane (10–20%), and minor amounts of butenes, together with isobutylbenzene (10%) and *n*-butylbenzene (20%), respectively, due to the slower oxidation (eq. 4) of primary radicals and competition from other facile radical reactions (eq. 6). Esters are significant but minor products (1–10%).

We postulate that there is a unity of mechanism which pertains to decarboxylation of carboxylic acids generally.^{1–4, 12} The spectrum of products obtainable with diverse acids is attributable to varying efficiencies of the initiation and particularly the propagation steps with the structure of the acid. The roles of ligand transfer and electron transfer in the oxidation steps (4 and 5), and the preparative value of Pb(IV) decarboxylations in the presence of Cu salts, will be presented later.

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(12) In following studies we hope to demonstrate the general applicability of mechanism 2–6 to decarboxylations of other acids (with the possible exception of formic acid) and a related mechanism to other substrates.

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Reactions of Thermal Carbon Atoms¹

Sir:

We have bombarded 99.999% zone-refined benzene frozen on a liquid nitrogen cooled surface with carbon fragments from carbon vapor.² Gas chromatographic analysis of the irradiated benzene shows toluene and cycloheptatriene to be among the reaction products. It seems most probable that these products result from the reaction of benzene with thermal carbon atoms.

The carbon vapor was obtained by electrically heating a spectrographic quality carbon rod mounted centrally in the 500-ml. bombardment flask, which was evacuated to a pressure of 0.1 to 1.0 μ during all bombardments. Benzene (*ca.* 0.003 ml.) was introduced into the flask as vapor mixed with He so as to be diffusion blocked. After a 1-min. period for condensation of benzene on the liquid nitrogen cooled walls, any uncondensed benzene and the He were pumped off. The rod was then turned on and the benzene bombarded with carbon vapor for 180 sec. All experiments consisted of 20 such successive bombardments. In some experiments the benzene was vaporized and collected in a cold finger between each bombardment. In others it was not vaporized until all 20 bombardments had been run. After completion of the 20 bombardments, the 0.06 ml.

(1) (a) This research was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research, Grant No. AF-AFOSR-245-65; (b) research sponsored by U. S. Army Research Office (Durham) Grant No. DA-ARO(D)-31-124-G-271.

(2) The composition of carbon vapor under equilibrium and non-equilibrium conditions has been extensively investigated.³ Under non-equilibrium conditions the relative surface evaporation rates of the three most abundant constituents of carbon vapor, C₁, C₂, and C₃, are 1.0, 1.0, and 1.6³⁰ at 2500°K.

(3) (a) R. J. Thorn and G. H. Winslow, *J. Chem. Phys.*, **26**, 186 (1957); (b) J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *ibid.*, **31**, 1131 (1959); (c) R. P. Burns, A. J. Jason, and M. G. Inghram, *ibid.*, **40**, 1161 (1964).