1-Chlorocyclopentene was prepared from cyclopentanone and phosphorus pentachloride following the procedure reported by Mousseron and Jacquier.[23] The product was obtained in a 28% yield as a clear colorless liquid, bp 49° (100 mm), $n^{25}\text{D}$ 1.4632 (lit.[23] bp 115° (760 mm), $n^{25}\text{D}$ 1.4637). The nmr spectrum was consistent with the desired structure, exhibiting a multiplet at τ 4.43 and two multiplets at τ 7.60 and 7.98, relative areas 1:4:2.

Formation of Vinyl Sodio and Potassio Compounds. The preparation of 1-sodiocyclopentene is given as a typical example of this type of reaction. A dispersion of sodium (4.6 g, 0.2 g-atom) was formed in the usual manner and cooled to 0°. 1-Bromocyclopentene (14.7 g, 0.1 mole) was slowly dripped into the rapidly stirring mixture during about 30 min, and the resulting mixture was allowed to warm to room temperature. After stirring for 30 min, one-third the volume of the dispersion was removed and carbonated, giving 2.1 g (~57%) of crude cyclopentene-1-carboxylic acid (see Table III).

Competition Experiments. The conditions used for competition experiments were the same as in the normal metalation reactions, with the total molar quantity of olefin present remaining the same and being equally divided between the two olefins used.

Acknowledgment. The authors gratefully acknowledge the assistance of L. H. Sickman, Jr., in this work.

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[23] M. Mousseron and R. Jacquier, *Bull. Soc. Chim. France*, 648 (1950).

Free Radicals in Thermal and Photochemical Oxidative Decarboxylations with Lead(IV)

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Abstract: The rates and products of decarboxylation of acids by Pb(IV) acetate differ widely according to their structure. Tertiary and α-aralkyl acids are readily decarboxylated and afford alkene and ester as products of oxidation in high yields, in contrast to primary and secondary aliphatic acids. Effect of inhibitors and scavengers and detection of radicals by electron spin resonance indicate that the mechanism of decarboxylation is the same for all these classes of acids. A free-radical chain sequence (eq 1 and 2) is involved. The relative rates of oxidation of alkyl radicals by Pb(IV) largely determine the distribution of products, being fastest with tertiary and related radicals. The photochemical reaction at 30° is equivalent to a thermal reaction at 80° and in most cases affords better yields of the same products. High quantum yields indicate an efficient chain reaction in the decarboxylation of tertiary acids.

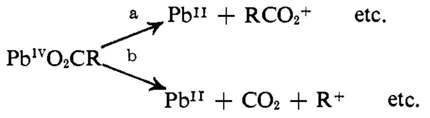
Lead tetraacetate[1] is a reagent widely applied in organic oxidations.[2] Mechanisms by which oxidation occurs are not completely established, and particularly germane is the nature of the Pb^{IV}–Pb^{II} transformation and the role of free radicals. We have chosen the oxidative decarboxylation of acids to examine these questions.

In an earlier study[3] we demonstrated that oxidative decarboxylation of *n*-valeric, isovaleric, and 2-methylbutyric acids by Pb^{IV} acetate proceeded *via* a free-radical chain mechanism involving butyl radicals. The chain propagation sequence (eq 1 and 2) was proposed as an important part in this homolytic process.[4]

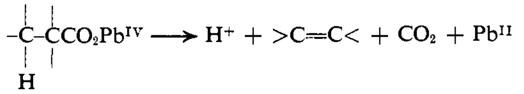
$$\text{Bu}\cdot + \text{Pb}^{\text{IV}}\text{O}_2\text{CBu} \longrightarrow [\text{Bu}^+] + \text{Pb}^{\text{III}}\text{O}_2\text{CBu} \qquad (1)$$

$$\text{Pb}^{\text{III}}\text{O}_2\text{CBu} \longrightarrow \text{Pb}^{\text{II}} + \text{CO}_2 + \text{Bu}\cdot \quad \text{etc.} \qquad (2)$$

An alternative formulation for the mechanism of oxidative decarboxylation by Pb^{IV} is a nonchain process which denies alkyl radicals as vital intermediates. A variety of such heterolytic mechanisms has been presented to accommodate the formation of alkenes and esters. These mechanisms are distinguished from the radical chain sequence proposed above in that the Pb^{IV} carboxylate is considered to undergo a discrete two-equivalent change from Pb^{IV} to Pb^{II}. For discussion here it is not pertinent whether such a direct Pb^{IV}–Pb^{II} transformation occurs *via* heterolysis of the ligand–Pb bond to form oxonium[5] or carbonium ions[6] (eq 3), or by a synchronous β elimination to form alkenes[7] (eq 4).



$$\text{Pb}^{\text{IV}}\text{O}_2\text{CR} \begin{array}{l} \xrightarrow{a} \text{Pb}^{\text{II}} + \text{RCO}_2^{+} \quad \text{etc.} \\ \xrightarrow{b} \text{Pb}^{\text{II}} + \text{CO}_2 + \text{R}^{+} \quad \text{etc.} \end{array} \qquad (3)$$



$$-\underset{\text{H}}{\overset{|}{\underset{|}{\text{C}}}}-\overset{|}{\underset{|}{\text{C}}}\text{CO}_2\text{Pb}^{\text{IV}} \longrightarrow \text{H}^+ + {>}\text{C}{=}\text{C}{<} + \text{CO}_2 + \text{Pb}^{\text{II}} \qquad (4)$$

The question of a homolytic or a heterolytic reaction has frequently remained unresolved because of the unequivocal observation of both radical and ionic characteristics in reactions of Pb^{IV} under differing conditions. Thus, a variety of functional groups other than carboxylic acids are readily oxidized by Pb^{IV} acetate. These include alcohols, glycols, alkenes, arenes, and various derivatives of amines. In a number of these cases, a step involving a direct Pb^{IV}–Pb^{II} has been speculatively included in the mechanism, and, indeed, a good case can be made for such two-equivalent processes.[8]

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[1] Hereafter referred to as Pb^{IV}.

[2] R. Criegee, "Oxidation in Organic Chemistry," K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, Chapter V.

[3] J. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965).

[4] Except where it is pertinent to the discussion, no attempt will be made to include all of the coordination about the Pb atom.

[5] W. Mosher and C. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

[6] E. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963).

[7] G. Buchi, R. Erickson, and N. Wakabayashi, *ibid.*, **83**, 927 (1961).

Our limited selection of carboxylic acids in the earlier study leaves open the possibility that there may be such another mechanism for oxidative decarboxylation which does not involve a radical chain mechanism. In particular, it is conceivable that a two-equivalent mechanism be applicable to tertiary, allylic, or benzylic acids which are known to be particularly prone to undergo facile decarboxylation in the presence of Pb^{IV}. These acids are also those which could yield reasonably stable carbonium ions, and may derive an optimum driving force from a two-equivalent heterolysis (eq 3b).

In this context, *exo*- and *endo*-bornane-2-carboxylic acids were recently found to decarboxylate with Pb^{IV} to a variety of products derived from the 2-bornyl cation.[9] No evidence for bornyl radicals could be adduced, and the authors concluded that either a two-equivalent mechanism or rapid successive one-electron oxidations obtained.[10]

In this report we wish to assert the generality of the radical chain mechanism (eq 1 and 2) as it also applies to a variety of tertiary and other easily decarboxylated acids. We hope to demonstrate the primacy of free alkyl radicals as vital links in the chain mechanism and to discuss the nature of the oxidation of tertiary and other alkyl radicals by Pb^{IV} (eq 1).

Results

Thermal Decomposition of Tertiary Acids with Pb^{IV}. Pivalic Acid. In a system from which oxygen had been removed by flushing with argon, the decarboxylation of pivalic acid in benzene at 81° yielded 48% isobutylene, 9% *t*-butyl acetate, 8% *t*-butyl pivalate, and 0.4% *t*-butylbenzene.[11] No isobutane (<0.1%) could be detected. The same reaction conducted in a freeze–thaw evacuated and sealed glass ampoule yielded the same products with virtually identical distribution.

$$(CH_3)_3CCO_2H + Pb^{IV}O_2CR \longrightarrow [(CH_3)_2C{=}CH_2 + (CH_3)_3CCO_2R] + CO_2 + 2H^+ + Pb^{II}$$

When a small amount (3–7 mole %) of oxygen was introduced into the argon-flushed decarboxylation, the reaction was instantly interrupted, as denoted by the cessation of gas evolution. After a brief inhibition period (15–30 min), retarded decarboxylation was observed until completion of the reaction. The effect on the progress of the reaction was attended by a remarkable deficiency of normal oxidation products and the presence of products derivable from radical–oxygen reactions. The effect of oxygen was similar but not identical with that observed with primary and secondary acids examined previously.[3] Thus, a long inhibition period followed by resumption of the reaction at its original rate was not observed with this tertiary acid.

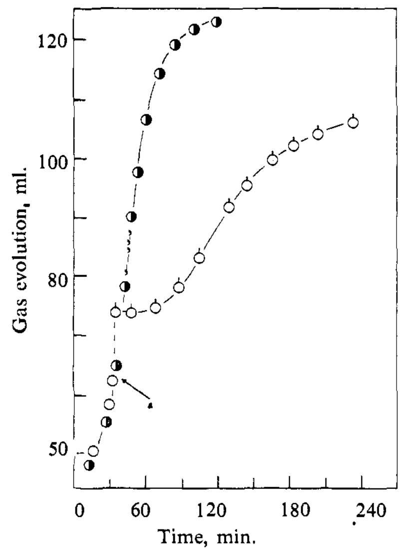

Figure 1. Thermal (81°) decarboxylation of 2,2-dimethylbutyric acid (9.1 *M*) in benzene with 0.19 *M* lead(IV) acetate: ◑, normal evolution; ȯ, evolution after 10 ml of oxygen introduced at a.

Pyridine catalyzed the pivalic acid decarboxylation. Besides producing an increase in rate, the addition of pyridine also resulted in an increase in the over-all yield of products with approximately the same distribution.

Cupric ion, however, had little effect on the reaction. The addition of cupric acetate did not influence the rate of decarboxylation and had only a minor effect on product distribution.

Oxygen had the same effect on the reactions to which Cu(II) or pyridine were added, as it did on the reaction without additives, *i.e.*, reaction progress was impaired and the yield of normal oxidation products was reduced.

2,2-Dimethylbutyric Acid. The decarboxylation of 2,2-dimethylbutyric acid in benzene at 81° in an argon-flushed system produced a 50% yield of a 1:1 mixture of 2-methylbutene-1 and 2-methylbutene-2. Smaller amounts of *t*-amyl esters (9%) and *t*-amylbenzene (0.3%) were also produced. No isopentane (<0.1%) could be found.

The same reaction, to which 10 mole % oxygen had been added, yielded only 28% olefin, 6% ester, and 0.4% *t*-amylbenzene. Along with the reduction in the yield of normal oxidation products, added oxygen produced the same retardation of gas evolution as was observed with pivalic acid (Figure 1).

2,2-Dimethylvaleric Acid. Although only the olefin products from the decarboxylation of 2,2-dimethylvaleric acid were examined quantitatively, the results of the above two tertiary acids indicated that olefins, the major products, were sufficient to establish the behavior of the reaction. The normal reaction at 81° in benzene yielded 42% 2-methylpentene-1 and 23% 2-methyl-

$$CH_3CH_2CH_2C(CH_3)_2CO_2H + Pb^{IV} \longrightarrow [CH_3CH_2CH_2(CH_3)C{=}CH_2 + CH_3CH_2CH{=}C(CH_3)_2] + 2H^+ + CO_2 + Pb^{II}$$

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(8) In principle, however, a detailed examination of whether a mechanism involves a two-equivalent or two successive one-equivalent changes is a moot point. If the latter involves rapid sequential changes, it cannot be distinguished from the former. Thus, eq 3 can be dissected into an initial homolysis to Pb^{III} and aroyloxy radical or an alkyl radical and CO_2, followed by a rapid electron transfer between the geminate pair, Pb^{III} and radical. For this reason, we will pursue this question only from an operational point of view and rely solely on experimental evidence to support one or the other.

(9) G. Gream and D. Wege, *Tetrahedron Letters*, 503 (1967).

(10) Their mechanism is a nonchain process[8] as distinguished from sequence 1–2 and ascribes unusual lifetimes to the bornyl radicals formed in its solvent cage with Pb^{III}. Such mechanisms have also been proposed for oxidations of alcohols by Pb^{IV}: D. Hauser, *et al.*, *Helv. Chim. Acta*, **47**, 1883, 1961 (1964). An alternative chain mechanism for oxidation of alcohols has been presented recently: W. Starnes, *J. Am. Chem. Soc.*, **89**, 3368 (1967).

(11) All yields are based on moles of product per mole of Pb^{IV} irrespective of whether they are derived by oxidative or nonoxidative means.

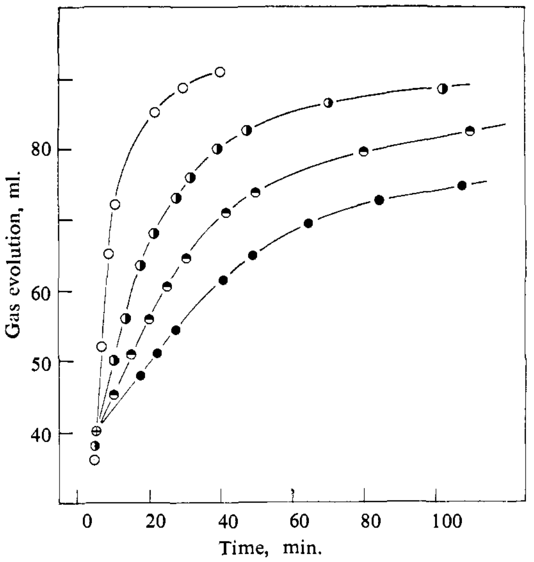

Figure 2. Effect of phenolic inhibitor on the thermal (81°) decarboxylation of triphenylacetic acid (0.1 *M*) in benzene–acetic acid with 0.09 *M* lead(IV) acetate: ○, normal evolution; 1.2, ◑; 2.4, ◒; and 4.7, ●; mole % ionol added at ⊕.

pentene-2. Pyridine and cyclohexene also catalyzed the decarboxylation of this acid and led to increased yields of methylpentenes. Isohexane was a minor product formed only in those decarboxylations carried out in the presence of cyclohexene.

Effect of Oxygen. When the decarboxylations of the above tertiary acids were conducted in benzene at 82° with rapid magnetic stirring in a heavy-walled glass reactor (bomb) under 42 psig of oxygen, the reaction proceeded at only a fraction of the normal rate. Pivalic acid, which was completely decarboxylated in 30 min under oxygen-free conditions, consumed only 61% Pb^{IV} in 31 hr in a bomb reaction. Except for the high oxygen pressure, the reaction conditions were the same as those of the normal decarboxylations. The normal oxidation products were barely detectable, and the reaction produced, in good yield, products which are derivable from tertiary alkylperoxy and alkoxy radicals.

After 48 hr in the oxygen bomb, the decarboxylation of pivalic acid produced di-*t*-butyl peroxide (3%), acetone (9%), and *t*-butyl alcohol (78%) and complete reduction of Pb^{IV}. In separate bomb reactions, Pb^{IV} was only 25 and 61% consumed after 24 and 31 hr, respectively; the above products were produced in proportion to the amount of Pb^{IV} consumed. The material balance was excellent and we feel that these products were a result of lead(IV) reaction and were not those produced in some spurious manner.

Although the yields of peroxide and alcohol were directly related to the Pb^{IV} consumed, the yield of acetone was not. Increased Pb^{IV} consumption led to decreased yields of acetone. These results are attributed to a further reaction of acetone[12] with Pb^{IV}.

Both 2,2-dimethylbutyric and 2,2-dimethylvaleric acids produced results similar to pivalic acid. However, the relative yields of acetone (40–50%) and alcohols were reversed and only minor amounts of *t*-amyl (12%) and *t*-hexyl (14%) alcohols were formed in contrast to major amounts of *t*-butyl alcohol from pivalic acid.

Triphenylacetic Acid. The decarboxylation of triphenylacetic acid was examined in an attempt to demonstrate the intermediacy of free radicals in a system where a relatively stable carbonium ion might be most expected to exclude free-radical formation in favor of a one-step, two-equivalent decarboxylation. The reactions were conducted in 50 vol. % benzene–acetic acid solution at 61 and 81° with acid/lead(IV) ratios of 1.06–1.36. No attempt was made to isolate triphenylmethyl ester products from the reactions because of their hydrolytic susceptibility. Reaction mixtures were completely hydrolyzed and the product isolated as triphenylcarbinol.

The decarboxylation of triphenylacetic acid at 81° in an argon-flushed system was quite rapid, even in the presence of the acetic acid required to maintain homogeneity. CO$_2$ evolution was complete after 30 min. The rate of CO$_2$ evolution from a similar reaction from which atmospheric oxygen was not removed was noticeably less rapid; more than 100 min were required for complete reaction. The addition of 9% oxygen to a flushed decarboxylating reaction did not produce inhibition, but retardation was observed. Completion of CO$_2$ evolution required 150 min. Thus, oxygen did not effect complete inhibition, but retardation. After hydrolysis of the reaction mixtures, 84–89% triphenylcarbinol was isolated from these reactions.

$$\mathrm{Ph_3CCO_2H + Pb^{IV}O_2CR \longrightarrow Ph_3CO_2CR + Pb^{II} + CO_2 + H^+}$$

The effect of oxygen observed in the decarboxylation of triphenylacetic acid was similarly produced by the addition of *p*-cresol or ionol (2,6-di-*t*-butyl-*p*-cresol) to the reaction. The addition of 1.2, 2.4, and 4.7 mole % ionol to separate reactions effected retardation of the rate of gas evolution in proportion to the amount of ionol added, without changing the total amount of gas evolved (Figure 2). Addition of 1.2 mole % ionol reduced the rate from 7.5 ml of CO$_2$/min to 2.0 ml/min.

Except for longer reaction time, decarboxylations conducted at 61° exhibited behavior similar to that observed at 81°. Reactions were *retarded* by either resident oxygen or by oxygen deliberately added to a flushed system. CO$_2$ evolution in an oxygen-free reaction was complete after 3 hr, while reactions containing oxygen were incomplete after 7 hr.

In a separate reaction, the decarboxylation was conducted at 82° in a stirred heavy-walled glass reactor (bomb) under 42 psi of oxygen, in an attempt to isolate trityl peroxide from the reaction. Except for the high oxygen pressure, conditions were identical with those employed in the reactions above. After 27 hr all Pb^{IV} had been consumed. While 89% triphenylcarbinol (after hydrolysis) was isolated from the reaction, no trityl peroxide could be detected. Trityl peroxide was similarly absent in bomb reactions conducted under 45 psi of oxygen at 61°. Although these reactions failed to yield the desired peroxide, they did serve to magnify the effect of oxygen on the progress of the reaction. While the normal oxygen-free reaction was complete in 3 hr, only 74% of the lead(IV) was consumed after 20 hr under O$_2$ pressure, and only 93% was consumed after 43 hr.

α,α-Dimethylphenylacetic Acid. Lead tetraacetate easily effected the oxidative decarboxylation of α,α-dimethylphenylacetic acid, a tertiary benzylic acid, in

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

benzene–acetic acid. After 1 hr at 81° the reaction yielded 87–90% CO_2, 12–13% α-methylstyrene, 52–61% α-cumyl acetate, and 3–4% α-cumyl alcohol. The

$$\mathrm{Ph(CH_3)_2CCO_2H} + \mathrm{Pb^{IV}O_2CR} \longrightarrow [\mathrm{Ph(CH_3)C{=}CH_2} + \mathrm{Ph(CH_3)_2CO_2CR}] + \mathrm{Pb^{II}} + \mathrm{CO_2} + 2\mathrm{H^+}$$

alcohol resulted from hydrolysis of the corresponding acetate during the acidic aqueous work-up. No cumene, the reduction product, dicumene (3,4-diphenyl-3,4-dimethylbutane), the radical coupling product, or α-methylstyrene dimer (2,4-diphenyl-4-methylpentene-2) was observed. Since no toluene was observed among the products, acetic acid was not competitively decarboxylated in this system.

Unlike the decarboxylation of the tertiary aliphatic acids, the decarboxylation of this tertiary benzylic acid was catalyzed both by pyridine and by cupric acetate. The more rapid, catalyzed reactions produced a higher yield of oxidation products (88%–90%) but produced little or no change from the distribution observed in similar uncatalyzed homogeneous reactions.

The reaction is somewhat complicated by the facile reaction of lead tetraacetate with α-methylstyrene to afford phenylacetone,[13] which was observed among the products from all reactions, and the relative amount increased in the less rapid reactions.

Although the reaction was understandably less rapid, the decarboxylation proceeded equally well at 61°. The yields of products and their distribution were virtually independent of temperature. Pyridine and cupric acetate exhibited the same catalytic effect at the lower temperature. At 81° retardation by oxygen was unnoticeable in the facile pyridine-catalyzed decarboxylation and minor in the uncatalyzed reaction. At 61°, however, the rate was about one-fourth as fast and oxygen inhibited the decarboxylation for prolonged periods.[14]

Under oxygen pressure, α-cumyl acetate and α-methylstyrene were no longer important products. Acetophenone, formed in low yields, was the only other product identified in a slow reaction. The latter is derived from the disproportionation and cleavage of an α-cumylperoxy radical.[15]

Diphenylacetic Acid. Diphenylacetic acid was decarboxylated smoothly by Pb^{IV} at 81° in benzene–acetic acid in an oxygen-free system. Although the variations were minor, the rate of the reaction and the yield of the resulting benzhydryl acetate were inversely related to the acetic acid concentration.

The presence of oxygen had a remarkably deleterious effect on the progress of the reaction. While a decarboxylation in 20:10 benzene–acetic acid (by volume) from which oxygen had been removed by flushing with nitrogen was complete in 6.5 hr, an identical unflushed reaction required 48 hr for complete CO_2 evolution. If oxygen (3.6 mole %) was introduced into a reaction in progress, the rate of gas evolution was instantly reduced to a small fraction of its original rate. The reaction continued to produce CO_2 at the reduced rate for more than 40 hr until all the Pb^{IV} had been consumed, If after 2 hr the oxygen was purged (by removing the reaction vessel from the bath, cooling, reflushing the system with nitrogen, and returning the reaction vessel to the bath), the reaction proceeded on the same course described for the oxygen-free system.

In addition to benzhydryl acetate (85–90%), small amounts of benzhydrol (0.2%) and benzophenone (1%) were observed as products. The alcohol resulted from

$$\mathrm{(C_6H_5)_2CHCO_2H} + \mathrm{Pb^{IV}O_2CR} \longrightarrow \mathrm{(C_6H_5)_2CHO_2CR} + \mathrm{Pb^{II}} + \mathrm{CO_2} + \mathrm{H^+}$$

partial hydrolysis of the acetate during the work-up. The hydrolysis of diphenylmethylene diacetate was responsible for the ketone and was formed either *via* α-acetoxylation of the acid and subsequent oxidative decarboxylation of the acid or *via* acetoxylation of benzhydryl acetate.

While small amounts of oxygen drastically affected the rate of the reaction, little or no effect was observed on products. This was in striking contrast to the effect of oxygen on the decarboxylation of tertiary aliphatic acids where similar amounts of oxygen were found to reduce profoundly the yield of normal oxidation products. When the uncatalyzed decarboxylation was conducted at 82° in a glass bomb under 40 psi of oxygen, the rate of the reaction was extremely slow. While a similar oxygen-free reaction was complete in 4.8 hr and one to which 2.5 mole % oxygen had been added consumed 97% Pb^{IV} in 23 hr, the reaction under oxygen pressure had consumed only 57% of the Pb^{IV} after 48 hr. However, the latter reaction did produce 19% benzophenone and 2.4% benzhydrol in addition to 69% benzhydryl acetate (based on Pb^{IV} consumed). Thus, the influence of oxygen on products of the benzhydryl system is apparent only at high pressures.

Photochemical Decomposition of Acids with Pb^{IV}[16]

Tertiary Aliphatic Acids. The decarboxylation of tertiary aliphatic acids by Pb^{IV} is effectively induced by light. The irradiation with 3500-A light of a benzene solution of Pb^{IV} and tertiary acid of the same composition as that employed in the thermal reactions resulted in rapid oxidative decarboxylation. Whereas complete reduction of Pb^{IV} thermally (81°) required 30–90 min, photolytically the reaction of identical oxygen-free solutions was complete in less than 10 min. Photolytic decarboxylation produced similar, although not identical, products in higher yield than was observed thermally.

The photolytic decarboxylation of pivalic acid by lead tetraacetate yielded 74% isobutylene, 15% *t*-butyl acetate, and 8% *t*-butyl pivalate. While the thermal reaction produced a small amount of *t*-butylbenzene (0.4%) and no (<0.1%) alkane, no *t*-butylbenzene and a small amount of isobutane (0.5%) resulted from the photolytic decarboxylation. While only a 67% material balance of the *t*-butyl moiety was observed in the thermal reaction, the over-all yield photolytically was virtually quantitative.

2,2-Dimethylbutryic acid was photolytically decarboxylated by Pb^{IV} and yielded 2-methylbutene-1

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[13] H. Hock and H. Kropf, *Ber.*, **56**, 1681 (1958).

[14] This striking effect is not necessarily due to the ineffectiveness of oxygen as an inhibitor at the higher temperature. In systems which are undergoing rapid decarboxylation oxygen is swept out of solution.

[15] M. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **16**, 113 (1951).

[16] Others have examined the photochemical decomposition of Pb^{IV} carboxylates: (a) V. Franzen and R. Edens, *Angew. Chem.*, 73, 759 (1961); (b) K. Heusler, H. Labhart, and H. Loeliger, *Tetrahedron Letters*, 2847 (1965).

(44%), 2-methylbutene-2 (36%), *t*-amyl acetate (8%), and *t*-amyl 2,2-dimethylbutyrate (4%). The small amount of *t*-amylbenzene (0.3%) produced in the thermal reaction was noticeably absent in the photolytic decarboxylation. As with pivalic acid, while no alkane was observed thermally, the photolytic reaction produced 0.5% isopentane. The photolytic decarboxylation afforded more than 90% product derived from the *t*-amyl group, while only 58% was observed thermally.

As with the previous two tertiary acids, the photolytic decarboxylation of 2,2-dimethylvaleric acid with lead tetraacetate yielded a small amount (*ca.* 0.5%) of alkane, isohexane, although none (<0.1%) was observed thermally. In addition, photolysis yielded 54% 2-methylpentene-1 and 28% 2-methylpentene-2. The ester products were not examined.

While accurate quantum yield measurements on the system were not undertaken, preliminary results employing uranyl oxylate actinometry indicate a chain length of 200. This value is sharply diminished by traces of oxygen.

α,α-Dimethylphenylacetic Acid. Like that of tertiary aliphatic acids, the oxidative decarboxylation of α,α-dimethylphenylacetic acid by Pb^{IV} was efficiently induced by light. Irradiation of benzene–acetic acid solutions, of the same composition as those employed in the thermal decarboxylations, resulted in complete reduction of Pb^{IV} in 30–35 min. Reaction time was somewhat longer in the case where oxygen was not removed from the quartz photolysis tube by sweeping with nitrogen. The photolysis at 3500 A and 30° produced a mixture containing 78% α-cumyl acetate and 11% α-methylstyrene whose composition is the same as an equivalent reaction conducted thermally.

Diphenylacetic Acid. The irradiation of benzene–acetic acid solutions of diphenylacetic acid and Pb^{IV} was complete in less than 1 hr, whereas complete reduction of Pb^{IV} thermally (81°) in the absence of a catalyst required 4.8 hr. The photolytic decarboxylation of diphenylacetic acid was somewhat less rapid than that of the tertiary aliphatic acids discussed earlier because of a lower acid/Pb^{IV} ratio and the acetic acid required as solvent to maintain homogeneity.

The same high yield of oxidative decarboxylation products observed thermally (81°) was produced in the photolytic reaction. Beside the major product, benzhydryl acetate (91%), the oxygen-free photolytic reaction also produced small amounts of benzhydrol and benzophenone (1%) from hydrolysis of diphenylmethylene diacetate, which could be formed in the reaction *via* α-acetoxylation of the acid. In addition to the above products, the photolytic reaction also yielded a small amount (0.5%) of diphenylmethane which was not observed in the thermal reactions.

The photolytic reaction from which atmospheric oxygen was not removed by flushing with nitrogen produced less benzhydryl acetate and significantly higher yields of benzophenone and benzhydrol. Moreover, the time required for reaction was noticeably longer. Both observations were probably the result of the interaction of diphenylmethyl radical with oxygen.

Cyclohexanecarboxylic Acid. The decarboxylation of cyclohexanecarboxylic acid was examined photochemically at several wavelengths. The results are summarized in Table I and compared to an equivalent thermal reaction carried out in refluxing benzene.

Table I. Direct Comparison of Thermal and Photochemical Decarboxylations of Cyclohexanecarboxylic Acid with $Pb^{IV\,a}$

Method	Cyclohexane, %	Cyclohexene, %	Cyclohexyl acetate, %	Cyclohexyl cyclohexanecarboxylate, %	Phenylcyclohexane, %
Thermal	14	38	20	13	10
3500 A	22	28	9	4	2
2537 A	24	32	13	4	2

[a] In benzene solutions containing 0.26 *M* Pb^{IV} and 1.2 *M* cyclohexanecarboxylic acid. All yields presented as moles of product per mole of Pb^{IV} consumed.

If photolyses at 2537 A were carried out for extended periods, Pb^{II} carboxylates were decarboxylated further. Metallic Pb together with cyclohexane and cyclohexene were major products.

Electron Spin Resonance Studies. The electron spin resonance spectra of various Pb^{IV} carboxylates were examined by irradiating samples directly in the cavity of the spectrometer. Solutions were prepared under a variety of conditions including neat acid, benzene, or pyridine as solvent. If solutions were not degassed only the spectra of alkylperoxy radicals were readily obtained at room temperatures with the tertiary acids pivalic, 2,2-dimethylbutyric, 2,2-dimethylvaleric, and 2,2-dimethyloctanoic acids (singlet, g = 2.0152 external standard). No alkylperoxy radicals were observed with other acids such as valeric, isovaleric, 2-methylbutyric, vinylacetic, or cyclobutanecarboxylic acids. Upon extinction of the light the signal disappeared at a measurable rate and appeared on reirradiation.

Crystalline Pb^{IV} carboxylates derived from phenylacetic, pivalic, 2,2-dimethylvaleric, isobutyric, and *n*-butyric acids were prepared and sealed in quartz tubes after degassing at 1 μ for 1 hr. Upon irradiation in the esr cavity the singlet signal due to the alkylperoxy radical previously described was not observed.

Irradiation of crystalline lead(IV) trimethylacetate at 77°K gave an asymmetric broad four-line signal. The low-field line was the most intense one; the intensity of each line decreased with increasing field. A better defined signal could not be obtained. Upon raising the temperature of the irradiated sample to 177°K, there was no apparent change in the general features of this signal. However, the signal gradually broadened and flattened out as the temperature was brought to room temperature in increments of 30°. No signal was observable at room temperature with irradiation.

A benzene solution of Pb^{IV} acetate (*ca.* 0.1 *M*) and trimethylacetic acid (*ca.* 0.5 *M*) was prepared in a similar manner except that the acid dissolved in the benzene, after degassing by successive freeze–thaw cycles at 1 μ, was mixed with the solid Pb^{IV} *in vacuo*. Both of these solutions upon irradiation in the cavity of the esr spectrometer at 130–170°K displayed the same spectrum as described for solid Pb^{IV} trimethylacetate.

A solution prepared similarly from neat 2,2-dimethyloctanoic acid and Pb^{IV} acetate produced no detectable signals upon scanning the field while the sample was irradiated at room temperature, even for prolonged periods of time. This sample gave the appearance of decomposing during the irradiation as evidenced by bubbles of carbon dioxide being emitted from the sample during irradiation. The seal on the tube was broken and air admixed with the contents of the tube. Upon taking the spectrum of this solution, the singlet signal for alkylperoxy radicals was observed.

In view of our conflicting data with the elegant results recently published by Heusler, Labhart, and Loeliger,[16b] we have temporarily suspended further studies.

Discussion

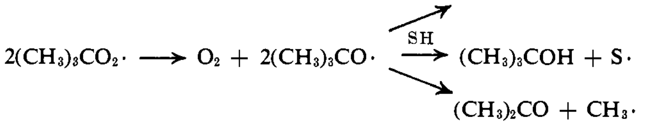
We have shown in this study that tertiary and α-aralkyl acids, which are distinguished from primary and secondary systems by their rapid rate of decarboxylation, are affected by the same factors designed to probe a radical chain mechanism. The unambiguous role of free radicals as *prime* intermediates in oxidative decarboxylation of acids[17] has been demonstrated in a variety of ways. These include: (a) inhibition of the reaction; (b) scavenging of the free radicals, (c) equivalence of the photochemical and thermal reactions, (d) high quantum yields, (e) detection of free radicals by electron spin resonance. In the chain mechanism (eq 1 and 2), the effect of structure of the acid on the rates and products of decarboxylation can be directly related to a process involving oxidation of alkyl radicals by Pb^{IV} (eq 1).

Effect of Inhibitors. Oxygen strongly inhibits the decarboxylation of primary and secondary pentanoic acids.[3] Tertiary aliphatic systems such as pivalic acid and 2,2-dimethylbutyric acid are also inhibited, but inhibition times are shorter by a factor of 5–10. The rates of decarboxylation increase with temperature and inhibition by oxygen at 60° becomes retardation at 80°. Cresol and 2,6-di-*t*-butyl-*p*-cresol in small amounts effect retardation at 80° in relation to their concentration without otherwise affecting the reaction.

The products derived from oxygen inhibition are clearly related to the interception of the alkyl radicals. Thus, pivalic and 2,2-dimethylbutyric acids in the presence of sufficient oxygen afford none of the usual products of oxidative decarboxylation.

t-Alkylperoxy radicals were readily observed by direct examination of the esr spectrum. Their chemical behavior is the same as those generated thermally from other unambiguous sources. Thus, *t*-butoxy radicals which result from disproportionation of *t*-butylperoxy radicals couple to di-*t*-butyl peroxide, fragment to acetone, and undergo hydrogen transfer to *t*-butyl alcohol.[18] The latter route is more important than fragmentation, but the higher homologs are more prone to fragment, and acetone is a major product.

$$(CH_3)_3C\cdot + O_2 \longrightarrow (CH_3)_3CO_2\cdot$$



$$2(CH_3)_3CO_2\cdot \longrightarrow O_2 + 2(CH_3)_3CO\cdot \begin{array}{l} \nearrow (CH_3)_3COOC(CH_3)_3 \\ \xrightarrow{SH} (CH_3)_3COH + S\cdot \\ \searrow (CH_3)_2CO + CH_3\cdot \end{array}$$

t-Amyl and *t*-hexyl radicals derived from the decarboxylation of dimethylbutyric and dimethylvaleric acids in the presence of oxygen produce major amounts of acetone, in accord with the established behavior of these radicals.[19] Furthermore, secondary and primary alkylperoxy radicals have shorter lifetimes than their tertiary counterparts,[20] and we were unable to detect these alkylperoxy radicals in esr studies at room temperature.

Triphenylacetic acid is readily decarboxylated by Pb^{IV} despite the absence of pyridine as catalyst. By the same token, oxygen and phenols only retard the decarboxylation even at 60°. Dimethylphenylacetic acid is retarded by oxygen at 80° and inhibited at 60°. Diphenylacetic acid is readily inhibited at 80°. Products derived from oxygen vary similarly with structure of the alkyl radical. Triphenylmethyl yields little if any product derived from oxygen, whereas diphenylmethyl yields benzophenone only at high oxygen pressures. Cumyl radical is completely trapped by oxygen.

These rather discordant results can be accommodated if the formation of the peroxy species of stable radicals is considered reversible. Recently Janzen, *et al.*,[21] have shown that trityl peroxy formation is highly reversible with a ceiling temperature (*i.e.*, $Ph_3CO_2/Ph_3C\cdot = 1$) of 75° at 1 atm in the solid phase. The heat of formation of tritylperoxy is −9 kcal/mole compared to −13 kcal/mole estimated for benzylperoxy radical.[22] Diphenylmethylperoxy is probably intermediate in stability. Similarly one would expect the activation energy for dissociation to increase from 10 kcal/mole for tritylperoxy to perhaps greater than 15 kcal/mole for benzylperoxy.

$$Ph_3C\cdot + O_2 \rightleftarrows Ph_3CO_2\cdot \qquad \Delta H = -9 \text{ kcal/mole}$$

The oxidation of trityl radicals by Pb^{IV} is rapid. When tritylperoxy radicals are formed reversibly, coupling and disproportionation of radicals as second-order processes are disfavored at low concentrations compared to the facile oxidation of trityl by Pb^{IV}. The higher yields of products derived from diphenylmethylperoxy radicals are also consistent with a less reversible system. The same applies in degree to allylperoxy radicals,[23] and the effect is diminished with cumylperoxy and benzylperoxy radicals. The latter yield acetophenone and benzaldehyde by cleavage and disproportionation, respectively.

Comparison of Thermal and Photochemical Decarboxylations. The thermal decarboxylation at 80° can be compared to the photochemical reaction at 30° in benzene. In both cases tertiary carboxylic acids yield alkenes and esters as products of oxidation. Alkybenzenes are minor products. Alkanes are absent from the thermal reaction and formed only in trace quantities in the photochemical decarboxylations. These results are compared in Table II.

In most cases, photochemical decarboxylation leads to higher yields of oxidation products than its thermal counterpart. This is particularly true of tertiary and

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(17) Formic acid may be an outstanding exception since it is readily oxidized by Pb^{IV} at room temperature. It merits further study. *Cf.* J. Halpern and S. Taylor, *Discussions Faraday Soc.*, **29**, 175 (1960).

(18) A. Factor, C. Russell, and T. Traylor, *J. Am. Chem. Soc.*, **87**, 3692 (1965).

(19) J. Bacha and J. Kochi, *J. Org. Chem.*, 30, 3272 (1965); *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(20) G. Russell, *ibid.*, **78**, 1047 (1956); **79**, 3871 (1957); **86**, 2364 (1964); *cf.* T. Traylor and C. Russell, *ibid.*, **87**, 3688 (1965); D. Carlson, J. Howard, and K. Ingold, *ibid.*, **88**, 4725 (1966).

(21) E. Janzen, F. Johnston, and C. Ayers, *ibid.*, **89**, 1176 (1967).

(22) S. Benson, *ibid.*, **87**, 972 (1965).

(23) J. Bacha and J. Kochi, *J. Org. Chem.*, in press.

Table II. Comparison of Thermal and Photochemical Decarboxylation

		Oxidation products			
Acid	Method	Alkene	Ester	Alkane	Alkylbenzene
Trimethylacetic	Thermal	49	17	0	0.4
	Photochemical	74	23	0.5	0
2,2-Dimethylbutyric	Thermal	49	9	0	0.3
	Photochemical	80	12	0.5	0
2,2-Dimethylvaleric	Thermal	65	..	0	..
	Photochemical	82	..	0.5	..
α,α-Dimethylphenylacetic	Thermal	13	65	0	..
	Photochemical	12	78	0.5	..
Diphenylacetic	Thermal		88	0	..
	Photochemical		91	0.5	..
Cyclohexanecarboxylic	Thermal	38	33	14	10
	Photochemical	28	13	22	2

Alkanes are also derived from the Pb^{IV} decarboxylation. Formally, alkane does not require the reduction of Pb^{IV} since loss of CO_2 from the acid could generate it. Direct decarboxylation of acids does not occur under these conditions and obviously Pb^{IV} plays an important role in the formation of alkanes.[24,25] We postulate that alkyl free radicals are the direct precursors and alkanes are formed by a subsequent hydrogen-transfer reaction. An examination of Table III reveals that yields of alkanes are inversely related to yields of oxidation products (alkenes, esters). Those alkyl radicals readily oxidized are less prone to form alkanes and *vice versa*. Thus, in decarboxylations of primary acids, alkanes are major products in contrast to minor quantities of alkenes and esters. The opposite pertains to tertiary and α-aralkyl acids.[25]

Table III. Product Distribution from Thermal Decarboxylation of Selected Acids with Pb(IV) in Benzene

	Alkene, %	Alkyl esters, %	Alkane, %	Alkylbenzene, %	Ref
Primary acids					
n-Valeric	3	12	25	21	3
Isovaleric	0.3	2	38	11	3
Hydrocinnamic	0.2	1	7	22	23
4-Phenylvaleric	...	...	4	54[a]	*c*
Secondary acids					
2-Methylbutyric	30	55	15	10	3
Isobutyric	9	13	24	...	5
Cyclohexanecarboxylic	38	33	14	10	This work
Bornane-2-carboxylic	50[b]	19[b]	0	0	9
Tertiary acids					
Pivalic	48	17	0	0.4	This work
2,2-Dimethylbutyric	49	9	0	0.3	This work
Apocamphane-1-carboxylic	...	...	...	56	*c*
α-Aralkyl acids					
Triphenylacetic		89–95	0	...	5, this work
Dimethylphenylacetic	13	65	0	...	5, this work
Diphenylacetic		88	0	...	5, this work
2-Phenylbutyric	5	90		...	23
Phenylacetic		62	<3	1.6	23

[a] Tetralin, a product of *intramolecular* aromatic substitution. 1,4-Diphenylbutane not stated. [b] Extensively rearranged *via* cationic ntermediates. [c] D. Davies and C. Waring, *Chem. Commun.*, 263 (1965).

other easily decarboxylated acids. Thus, a material balance based on the alkyl moiety of greater than 90% can be obtained with such acids as pivalic, dimethylbutyric, dimethylvaleric, dimethylphenylacetic, and diphenylacetic acids. The corresponding thermal reactions afforded 10–20% lower yields of the same products.

The difference between thermal and photochemical decarboxylations is not distinguishable merely by an examination of the distribution of alkenes and esters as products.

Oxidation of Alkyl Radicals by Pb^{IV}. The standard reaction for oxidative decarboxylation can be represented by eq 4a. An examination of the results of

$$nRCO_2H \longrightarrow R_{ox} + CO_2 + 2H^+ + 2e \qquad R_{ox} = \text{alkene } (n = 1),\ \text{ester } (n = 2) \tag{4a}$$

Pb^{IV} decarboxylations of a variety of acids indicates that over-all yields of *oxidation products decrease* from tertiary to secondary to primary aliphatic acids. The effect is less pronounced with α-aralkyl acids. Some of the results are summarized in Table III.

The typical free-radical product butane is formed in 25% yield from the primary valeric acid and is less (15%) from the secondary 2-methylbutyric acid. Isobutane is a major product (38%) from the primary isovaleric acid; however, it is absent (<0.1%) from the tertiary pivalic acid. Similarly no isopentane or isohexane was detected from the decarboxylation of dimethylbutyric or dimethylvaleric acid, respectively. Cyclohexane constitutes 14% of the products from cyclohexanecarboxylic acid, but no triphenylmethane, cumene, or diphenylmethane could be detected in the thermal decarboxylation of triphenylacetic, dimethylphenylacetic, or diphenylacetic acid, respectively. Minor amounts of these products can be derived in the presence of efficient hydrogen donors (cyclohexene) or in photochemically induced reactions in which higher steady-state concentrations of radicals prevail.

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(24) The Pb^{IV} stoichiometry in the formation of alkane depends on the fate of radicals derived from hydrogen abstraction. If they dimerize the chain reaction will be retarded and two alkanes are formed per Pb^{IV}. If they are oxidized by Pb^{IV}, one alkane is derived from each Pb^{IV}. Compare S· in eq 6.

(25) An exception in Table III is apocamphane-1-carboxylic acid which generates a *bridgehead* tertiary radical.

We ascribe the distribution of the alkyl moiety among oxidation products (alkenes, esters) and alkanes to its relative ease of oxidation (eq 5) compared to hydrogen transfer (eq 6).

$$R\cdot \left[\begin{array}{ll} \xrightarrow{Pb^{IV}} [R^+] + Pb^{III} & (5) \\ \xrightarrow{SH} RH + S\cdot & (6) \end{array}\right.$$

In the gas phase, the ionization potential of alkyl radicals decreases in the order: primary (8.3–8.7 ev) > secondary (7.7–7.9 ev) > tertiary (7.1–7.4 ev).[26] The high yields of oxidation products from tertiary radicals are consistent with their low ionization potentials. Product distribution is a rather sensitive means of determining relative rates of competitive reactions such as eq 5 and 6.

Acids can be classified according to their rates of decarboxylation and yields of oxidation products. Accordingly, these can be employed as a qualitative measure of the rate of oxidation of radicals by Pb^{IV} (eq 5). Alkanes as products are symptomatic of an inefficient oxidation step. On this basis triphenylmethyl is among the most readily oxidized radicals. The others are in decreasing order: cumyl, *t*-alkyl, benzhydryl, α-phenylalkyl, cyclohexyl, *sec*-butyl, *n*-butyl, and isobutyl. In the following paper[23] we hope to elaborate further on the effects of structure on the ease of oxidation of free radicals by Pb^{IV} and Cu^{II}.

The products of oxidation are dependent on the alkyl moiety. We postulate that alkenes and esters arise *via* carbonium ions from electron transfer between alkyl radicals and Pb^{IV}. Factors which determine the partitioning of carbonium ions between alkenes and esters have not yet been resolved. Comparison of these systems to more conventional routes to carbonium ions may aid in these studies.

Absence of alkane in oxidative decarboxylation, *per se*, cannot be used to argue against the presence of free alkyl radicals.[9] Carbonium ion behavior often observed in oxidative decarboxylations is attributed to oxidation of radicals as first intermediates by electron transfer (eq 5).

The effectiveness of Cu^{II} as a catalyst further supports the discrimination shown by Pb^{IV} toward free alkyl radicals. Other studies have shown that Cu^{II} is an exceedingly efficient trap for alkyl radicals irrespective of whether they are primary, secondary, or tertiary.[27] The addition of Cu^{II} to the decarboxylation of the primary valeric and isovaleric acids drastically altered the course and increased the rate of reaction.[3] Its effect on the secondary 2-methylbutyric acid decarboxylation was less marked. On tertiary acids Cu^{II} produced no apparent effect on the rate. The catalysis by Cu^{II} in the decarboxylation of primary and secondary acids is attributed to the replacement of the relatively inefficient Pb^{IV} oxidation (eq 5) of primary and secondary alkyl radicals by the facile Cu^{II} oxidation (eq 7). This is followed by a Pb^{III} regeneration step (eq 8). With tertiary and α-aralkyl radicals such an intrusion by Cu^{II} in the chain sequence is unnecessary due to the facile oxidation of these radicals by Pb^{IV} itself.

$$R\cdot + Cu^{II} \longrightarrow [R^+] + Cu^{I} \qquad (7)$$

$$Cu^{I} + Pb^{IV} \longrightarrow Cu^{II} + Pb^{III} \quad \text{etc.} \qquad (8)$$

Yields of alkylbenzenes in general parallel the yields of alkanes, and are lower from tertiary acids than from primary and secondary acids. They are produced by homolytic substitution of alkyl radicals on benzene.[3,24] These reactions will be elaborated in subsequent studies.

Rates of Decarboxylation. The rates of thermal decarboxylation of acids vary with structure and generally decrease in the order: tertiary > secondary > primary. Thus, the relative rates of pivalic, 2-methylbutyric, and isovaleric are roughly 80:5:1 at 80° in benzene. Triphenylacetic and dimethylphenylacetic acids decarboxylate more rapidly than pivalic acid. Diphenylacetic acid loses CO_2 at approximately the same rate. Detailed kinetic studies were not carried out on these systems since it is known that metathesis precedes decomposition of the Pb^{IV} carboxylates. The equilibrium constants for these reactions have not been determined.

$$Pb^{IV}(OAc)_4 + nRCO_2H \rightleftharpoons Pb^{IV}(OAc)_{4-n}(O_2CR)_n + nHOAc$$

All of the tertiary acids we examined underwent thermal decarboxylation readily at 80°. With the exception of the readily decarboxylated triphenylacetic acid, the addition of pyridine enhanced both the rate of reaction and yields of oxidation products. In this regard, pyridine has the same effect as that observed earlier with primary and secondary acids.[3]

The thermal and photochemical decarboxylation of tertiary acids are equivalent. The chain character of the reactions is demonstrated by the high quantum yield ($\Phi \approx 200$) observed in the decarboxylation of pivalic and dimethylbutyric acids. Preliminary indications are that the decarboxylation of primary and secondary acids have significantly lower quantum yields. These are shown qualitatively by the longer times required for photolysis.

The kinetic chain length is one measure of the efficiency of a chain process and is given by the ratio of the rate of decomposition of Pb^{IV} to the rate of initiation (termination). The limiting step in the decomposition of Pb^{IV} is its oxidation of alkyl radicals (eq 5). We believe that this step also limits the kinetic chain length. The termination processes are not clear at present, but one important factor is related to hydrogen abstraction (eq 6), since we note that decarboxylations yielding alkane are also slow and have short kinetic chain lengths. Short-stopping by cyclohexene leads to increased rates due to subsequent facile oxidation of the cyclohexenyl radicals. We have not observed products directly related to the termination step. Neither coupled products from alkyl or solvent-derived radicals nor alkyl Pb carboxylates have been detected.

Competitive decarboxylation of several acids by Pb^{IV} shows that tertiary aliphatic and α-aralkyl acids lose CO_2 much faster than secondary or primary acids. The former can be decarboxylated in acetic acid as solvent. Dilute acetic acid solutions can be employed for secondary acids. Most primary aliphatic acids decarboxylate only two to three times faster than acetic acid and excess acetate should be avoided. The difference in competitive rates of decarboxylation of acids is related to the synchronous (multibond) fragmentation of the

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[26] F. Lossing and J. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959); R. Taubert and F. Lossing, *ibid.*, **84**, 1523 (1962).

[27] J. Kochi and R. Subramanian, *ibid.*, **87**, 4855 (1965).

Pb^{III} intermediate in step 2 of the proposed mechanism.

$$Pb^{III}(OAc)_2(O_2CR) \longrightarrow Pb^{II}(OAc)_2 + R\cdot + CO_2$$

A similar multibond cleavage is also operative in the initiation step involving fragmentation of the Pb^{IV} carboxylates.[3,28]

Electron Spin Resonance Studies. The Pb^{III} species proposed as an intermediate in oxidative decarboxylations has continued to elude us. Alkyl radicals and alkylperoxy radicals (in the presence of oxygen) have been detected by esr. No spectroscopic evidence is yet available for Pb^{III} which should be paramagnetic and exhibit a three-line pattern due to the presence of Pb^{207} with spin $^1/_2$ in 20% natural abundance. Heusler, *et al.*,[16b] reported the presence of alkyl radicals but made no mention of observing any other signals in the esr spectrum. Rexroad[29] reported detecting propyl radicals by irradiating tetrapropyllead at 77°K with γ irradiation. He, too, made no mention of signals ascribable to a Pb^{III} species. In this case the decomposition of tetrapropyllead to one propyl radical and tripropyllead(III), that is, stepwise decomposition, appears more reasonable than the direct decomposition to two propyl radicals and dipropyllead. Perhaps the reasons for our and the inability of others to observe this intermediate are (1) its absence, or (2) the extremely rapid, on the esr time-scale, exchange of the odd electron on the lead(III) with those on other lead species in the immediate vicinity, thus making any signal too broad to be observed. Perhaps at liquid helium temperatures, this exchange will be slow enough for the Pb^{III} to be observed. Flash photolysis of tetramethyllead[30] has yielded no additional information on this question. Further studies are in progress.

Experimental Section

Materials. All carboxylic acids were purified by distillation and/or recrystallization. Isolated cases required the conversion of the acid to its sodium salt and removal of nonacidic impurities by commonly employed extraction procedures. The purity of the acids was checked by gas chromatographic (glpc) analysis of the neat acids and/or their methyl esters.

Pivalic acid, bp 163–163.5°, and 2,2-dimethylvaleric acid, bp 203–204°, were generously donated by the Enjay Chemical Co. 2,2-Dimethylbutyric acid, bp 186–187°, was from K and K Laboratories, Inc. Triphenylacetic acid, mp 271–273°, and diphenylacetic acid, mp 148°, were from the Aldrich Chemical Co., and α,α-dimethylphenylacetic acid, mp 78°, was from Columbia Organic Chemicals Co. 2-Phenylbutyric acid, bp 135° (2 mm), mp 42–44°, hydrocinnamic acid, mp 48°, and cyclohexanecarboxylic acid, mp 30–31°, were from the Eastman Kodak Co. Benzene (thiophene-free) from Mallinckrodt Chemical Works was further purified by distillation. Glacial acetic acid, ACS reagent, Allied Chemical Corporation, was used as supplied.

Di-*t*-butyl peroxide was donated by the Shell Chemical Co. Triphenylmethyl peroxide, mp 185–186°, was prepared by the Gomberg procedure from triphenylmethyl chloride and zinc powder in benzene.[31]

Lead tetraacetate (G. F. Smith Chemical Co.) was recrystallized from glacial acetic acid containing 1–2% acetic anhydride and stored at −15° protected from light and moisture. Analysis by iodometric titration indicated 96–98% $Pb(OAc)_4$.

Thermal Oxidative Decarboxylations. Aliquots of a standardized solution of lead tetraacetate and carboxylic acid in benzene or individually prepared mixtures of reactants and solvent were decomposed as described earlier[3] in an oxygen-free system. Gas evolution, followed volumetrically with a mercury-filled eudiometer, provided a reasonable measure of the rate of the reaction.

In experiments employing a catalyst, it was added to the reaction as the last component prior to removal of oxygen from the system. In oxygen-inhibited decarboxylations, oxygen was introduced with a hypodermic syringe through the rubber septum either above or below the surface of the heated solution only after gas evolution had commenced. Changes produced in the rate of gas evolution were followed volumetrically.

Oxygen Bomb Reaction. The heavy-walled glass reaction vessel consisted of a 100-ml bulb fused to a glass pipe terminated with an O-ring seal. The reactor was charged by pipetting in a standardized Pb^{IV} solution or by preparing a solution within the vessel. A stainless steel cap equipped with a needle valve was attached to the vessel *via* a split steel collar. The reactor was pressured with 3 atm of oxygen, the cap-valve closed, and the reactor heated while stirring magnetically. The solution was protected from the steel cap and valve by a Teflon disk with a minute hole to permit the introduction of oxygen.

After several hours the reaction was cooled, the gases were vented into a mercury-filled gas buret, and the solution was diluted to a known volume with benzene and acetic acid. An aliquot of the reaction mixture was analyzed for unreacted Pb^{IV} by iodometric titration. The vented gas and the remaining solution were analyzed by gas chromatography.

Triphenylacetic Acid Decarboxylation. In a reaction vessel described earlier[3] were placed 1.00 g (3.48 mmoles) of triphenylacetic acid, 1.18 g (2.52 mmoles) of lead tetraacetate (96%), 15 ml of glacial acetic acid, and 15 ml of benzene. The vessel was connected to the eudiometer, the system purged of oxygen, and the reaction mixture heated at 81° with stirring. After gas evolution ceased, the reaction was cooled, and the solvent was removed by rotary evaporation to a slurry. Soluble Pb^{II} salts were removed by washing with water, and the insoluble material was stirred with 2% aqueous sodium carbonate. The resulting mixture was extracted with benzene, and the combined benzene extracts were washed with water and dried over sodium sulfate. After removal of the benzene, a sticky yellowish solid remained, which yielded 0.583 g of white crystalline triphenylcarbinol (89%), mp 160.5–161.5°, after washing with petroleum ether.

Retarded reactions were prepared as above except oxygen or solutions of ionol in benzene were introduced into the reaction vessel with a syringe after gas evolution began.

In an oxygen bomb reaction, 1.82 g (6.30 mmoles) of triphenylacetic acid, 2.73 g (5.92 mmoles) of lead tetraacetate (96%), and 3 ml each of glacial acetic acid and benzene were placed in the reactor. The mixture was stirred until homogeneous and 3 atm of oxygen was introduced. The reaction mixture was heated at 61° for 20 hr. The reaction vessel was cooled to 0°, and the gases were vented to mercury-filled burets. The reaction solution was diluted to 70 ml with benzene and acetic acid. Two 5-ml aliquots were titrated for Pb^{IV} iodometrically. The remaining solution was concentrated and to the resulting slurry was added a mixture of 150 ml of methylene chloride and 500 ml of saturated aqueous sodium bicarbonate. After the lead dioxide was removed by filtration the methylene chloride layer was washed with water and dried over sodium sulfate. Removal of the solvent yielded a sticky solid, which after washing with petroleum ether yielded 0.898 g (94%, based, on Pb^{IV} consumed) of colorless triphenylcarbinol, mp 161–161.5°, and very soluble in benzene or ethyl ether. Trityl peroxide, while soluble in methylene chloride, is insoluble in benzene or ether.

Photolysis. The photolytic decarboxylations were carried out in a Rayonet photochemical reactor (The Southern N. E. Ultraviolet Co.). Four 3500-A region lamps (3050 to 4150 A) were employed. Maximum capacity of the reactor is 16 lamps Aliquots (25 ml) of a standardized Pb^{IV} solution were transferred from the amber erlenmeyer flask in which the solutions were prepared to each of two 40 × 1 cm quartz tubes. The solution and the free space above were purged of oxygen by sweeping with a slow stream of nitrogen (or argon) for 20 min. The inert gas was introduced *via* a long glass capillary. After the tube was capped with a rubber septum, it was placed in the photochemical reactor which maintained an ambient temperature of 30 ± 1°. The lamps were arranged in a circular array and the tubes placed 10 cm away from the nearest lamp. The progress of the reaction was followed by the disappearance of the yellow color common to Pb^{IV} solutions containing traces of water. Upon completion, the solutions were water white.

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(28) Co^{III} carboxylates have also been postulated to decarboxylate by multibond cleavage: A. Clifford and W. Waters, *J. Chem. Soc.*, 2796 (1956); 794 (1966).

(29) W. Lyttle and H. Rexroad, *Proc. West Va. Acad. Sci.*, 32, 190 (1960).

(30) J. Clouston and C. Cook, *Trans. Faraday Soc.*, 54, 1001 (1958).

(31) M. Gomberg, *J. Am. Chem. Soc.*, 22, 757 (1900).

In those cases where cupric acetate was employed in the photolytic decarboxylations, a Cu^{II}–Pb^{IV} solution was prepared in an amber erlenmeyer flask. Aliquots of the homogeneous solution were then pipetted into the quartz tubes and the above procedure followed. The progress of these reactions could be followed by a color change from green to the blue of cupric acetate.

Analytical Procedures. The Pb^{IV} content of the starting lead tetraacetate and the unconsumed Pb^{IV} in the reaction mixtures were determined by iodometric titration according to the procedure of Kharasch and Friedlander.[32] Known components in the crude reaction mixtures were shown not to interfere with the analysis.

Reaction mixtures were analyzed by quantitative gas chromatography (glpc) using various internal standards which were previously calibrated against the individual reaction products. Identification of gas chromatographic peaks was verified by comparing their gas chromatography retention times with authentic compounds on at least two columns with different separation properties, *e.g.*, boiling point column and polar column. Moreover, identification was confirmed by chemical degradation of the reaction products. Typical cases are cited below.

Gas chromatographic analyses of gaseous and lower boiling hydrocarbons were performed on Case-constructed instruments, equipped with thermal conductivity detectors. Other analyses were performed on instruments with hydrogen flame ionization detectors: Aerograph, Model 200, dual column chromatograph, and Aerograph HiFy, Model 600-D.

Product Analysis from α,α-Dimethylphenylacetic Acid. Three principal products, α-methylstyrene, α-cumyl alcohol, and α-cumyl acetate, were identified by retention times which corresponded with those of authentic materials. Glpc analysis of the worked up reaction mixture after mild basic hydrolysis (0.5 *M* alcoholic KOH) revealed the absence of the ester component and a corresponding increase in the cumyl alcohol peak. Glpc analysis of the original reaction mixture or that resulting from basic hydrolysis yielded only one large peak corresponding to α-methylstyrene after treatment with dilute perchloric acid. While basic hydrolysis only saponified the ester, treatment with dilute mineral acid also caused dehydration. Hydrogenation of the original worked-up reaction mixture or the hydrolyzed mixtures moved the peak corresponding to α-methylstyrene to a new retention time corresponding to that of authentic cumene.

Acknowledgment. We wish to thank the Air Force Office of Scientific Research for a generous grant to support this research.

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[32] M. Kharasch, H. Friedlander, and W. Urry, *J. Org. Chem.*, **16**, 533 (1951).

The Mechanism of Reductive Elimination of *vic*-Dihalides by Chromium(II)

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Abstract: Reductive elimination of *vic*-dihalides and their analogs to alkenes by Cr^{II} is similar to reduction of alkyl halides and peroxides to alkanes. Kinetic studies show the mechanism of both involve multistep sequences. Stereochemical studies on *cis*- and *trans*-1,2-dibromocyclohexanes support Kray and Castro's hypothesis that a β-bromine has a neighboring group effect in the removal of the first halogen by ligand transfer to Cr^{II}. The resulting β-haloalkyl radicals yield alkenes in reductive eliminations by three competing processes. At low Cr^{II} concentrations, the β-bromoalkyl radical fragments to bromine atom and alkene, whereas at higher concentrations a β-bromoalkylchromium intermediate is postulated. *cis* elimination of $Cr^{III}Br$ or *trans* elimination of bromide and Cr^{III} are competing routes of heterolysis of the bromoalkylchromium complex. These studies are also supported by the extremely facile reductive elimination of β-haloacyl peroxides by Cr^{II}; Cr^{III} species and halide are quantitatively separated and identified by ion-exchange chromatography. A variety of other β-substituted alkyl halides also yields alkenes with Cr^{II}. Kinetic studies show that chloro-, tosyloxy-, hydroxy-, and acetoxyalkyl bromides are reduced much slower than vicinal dibromides and a significantly smaller neighboring group assistance by β-chloro, β-tosyloxy, β-hydroxy, and β-acetoxy groups in the removal of the initial bromine by Cr^{II} is indicated. Furthermore, fragmentation of the free radical and *trans* elimination of the alkylchromium intermediate are less important processes with β-chloro-, -hydroxy, and -acetoxyalkyl moieties compared to the β-bromo analog. The former appear to undergo reductive elimination exclusively by a concerted *cis* departure of a complexed Cr^{III} species from the β-substituted alkylchromium intermediate. On the other hand, the facile removal of a β-toxyloxy group may proceed largely *via* a transoid transition state.

A variety of organic halides are reduced by chromous compounds, which are commonly accessible and versatile reducing agents.[1] The rates of reduction and products are dependent on the structure of the organic halide. Among those classes of halides readily reduced are α-aralkyl halides, allylic halides, and α-halocarbonyl and cyano compounds. The former generally requires 2 moles of Cr^{II}[2] per mole of halide and affords products of bimolecular reduction (eq 1)[3] whereas the latter two types of halides undergo simple reduction (eq 2).[1]

$$2RX + 2Cr^{II} \longrightarrow R_2 + 2[Cr^{III},X^-] \qquad (1)$$

$$RX + 2Cr^{II}(SH) \longrightarrow RH + 2Cr^{III}(X^-,S^-) \qquad (2)$$

Alkyl and vinyl halides are practically unreactive to Cr^{II} and require prolonged exposure in order to effect even partial reduction. On the other hand, if Cr^{II} is complexed with ethylenediamine, the resulting species

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[1] For summaries, see (a) C. Castro and W. Kray, Jr., *J. Am. Chem. Soc.*, **85**, 2768 (1963); (b) L. Slaugh and J. Raley, *Tetrahedron*, 20, 1005 (1964); (c) J. Kochi and D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964).

[2] Unless specifically noted, chromous species are indicated as Cr^{II} without regard to the nature of solvation. Octahedrally coordinated chromous ion in these solvents is highly labile to substitution.

[3] J. Kochi and D. Buchanan, *J. Am. Chem. Soc.*, **87**, 853 (1965).