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Oxidative Decarboxylation of Carboxylic Acids

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The present state of studies on the decarboxylation of carboxylic acids by various oxidation systems is described and the dependence of the yield and composition of the reaction products on the structure of the carboxylic acid, the type of oxidant and its ligand environment, the nature of the solvent, and the reaction mechanism is considered. The intermediate involvement of radicals and ions, produced by successive one-electron transfer processes, in the formation of a wide variety of decarboxylation products is discussed.
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I. INTRODUCTION

The decarboxylation of carboxylic acids by the fusion of their alkali metal salts with caustic alkali and by the anodic oxidation of the acids and their salts (the Kolbe reaction) are familiar methods for the synthesis of alkanes. Together with alkanes, alkenes, alcohols, esters, and ethers are also formed in the Kolbe reaction and under certain conditions their yields can exceed that of alkanes[1-4].

The oxidative decarboxylation of carboxylic acids by transition metal salts and persulphates has been investigated vigorously in recent years. The practical value of the oxidative decarboxylation consists in the fact that, with the aid of this process, it is possible to obtain a series of important chemical products (alkanes, alkenes, ethers, esters, alcohols, alkyl halides, etc.). Decarboxylation takes place in the living organisms with participation of enzymes; some of these reactions are reversible and play an important role in the biological assimilation of carbon dioxide.

In the study of the mechanism of the oxidation process it is important to know whether the reaction takes place as a result of consecutive one-electron stages or as a two-electron process in a single stage. The yield and composition of the products depend in many respects on the kind of intermediate species formed—radicals and carbonium ions. Thus oxidative decarboxylation of carboxylic acids is a process in which the specific formation of the required synthetic products is closely related to the theoretical aspects of the oxidation reactions.

The decarboxylation of carboxylic acids by lead tetra-acetate has been used by a number of workers as a synthetic method[5-13]. The study of the mechanism of the decarboxylation of carboxylic acids was begun in the 1960s by Waters in aqueous media[14] and by Kochi in non-aqueous media[15]. The general mechanism of the decarboxylation reaction under the influence of oxidants[16] as well as anodic decarboxylation[4] is

represented as follows:

$$\mathrm{RCOOH} \begin{cases} \xrightarrow{-e,-H^+} \mathrm{RCOO^\cdot} \rightarrow \mathrm{R^\cdot} + \mathrm{CO_2} \\ \qquad\qquad\quad \downarrow -e \\ \xrightarrow{-2e,-H^+} \mathrm{R^+} + \mathrm{CO_2} \end{cases} \quad (1)$$

The radicals R· can react with hydrogen donors (for example, with the molecules of the solvent SH), giving rise to alkanes [Eqn.(2*c*)] and also dimerising with formation of R–R products [Eqn.(2*a*)] and disproportionating into alkanes RH and alkenes R(-H) [Eqn.(2*b*)]:

$$\mathrm{R^\cdot} \begin{cases} \xrightarrow[a]{\mathrm{R^\cdot}} \mathrm{R{-}R} \\ \xrightarrow[b]{\mathrm{R^\cdot}} \mathrm{RH} + \mathrm{R(-H)} \\ \xrightarrow[c]{\mathrm{SH}} \mathrm{RH} + \mathrm{S^\cdot} \end{cases} \quad (2)$$

Further oxidation of the radicals by metal salts leads to the formation of elimination products (alkenes) and substitution products (ethers, alcohols, and alkyl halides) via two-electron transfer mechanisms, which are known in inorganic chemistry as outer-sphere and inner-sphere mechanisms[16,17]:

$$\begin{array}{c} \mathrm{R^\cdot} + \mathrm{ML}_n \xrightarrow{a} [\mathrm{R^\cdot ML}_n] \xrightarrow{c} \mathrm{R^+} + \mathrm{ML}_{n-1} + \mathrm{L^{-1}} \\ \quad {}_{b}\swarrow \qquad\qquad d\downarrow \mathrm{An^-(L)} \\ \mathrm{R(-H)} + \mathrm{RL} + \mathrm{ML}_{n-1} \quad \mathrm{RA\ (RL),\ R\ (-H).} \end{array} \quad (3)$$

In conformity with the inner-sphere mechanism or the ligand-transfer mechanism, substitution takes place in the complex without the intermediate formation of carbonium ions [Eqns.(3*a*) and (3*b*)]. The mechanism can therefore also yield alkenes. In the outer-sphere, solvolytic, or classical carbonium ion mechanism, carbonium ions are formed as intermediates and their subsequent transformation leads to alkenes as a result of the loss of a proton or to substitution products as a result of the interaction of the carbonium ion with an anion [Eqns.(3*a*), (3*c*), and (3*d*)]. The yield and composition of the oxidative decarboxylation products depend significantly on the oxidant, the structure of the carboxylic acid, and the nature of the anions and the ligands associated with the metal cations.

The aim of the present review is to examine and, as far as possible, to survey the results of studies on the decarboxylation of carboxylic acids under the influence of various oxidation systems. The literature quoted in the review covers mainly the period of the last thirty years. The review does not include the decarboxylation reactions of silver salts of carboxylic acids, which take place under the influence of halogens in aprotic solvents and lead to alkyl halides (the Borodin–Hunsdiecker reaction) and to esters (the Simonini reaction). A review[18] has been devoted to the Borodin–Hunsdiecker reaction, after which there were few publications in the literature concerning this process. Furthermore, both these reactions are of a complex type and their mechanisms are not altogether clear. Their study is frequently complicated by heterogeneous reaction conditions.

Decarboxylation under the influence of electrophiles (bromine, H^+) in protic media, decarboxylation in basic solvents, and enzymatic decarboxylation, which has its specific features, have also been excluded from consideration. A monograph has been devoted to decarboxylation reactions leading to organometallic compounds[19] and we shall therefore confine ourselves to considering only the general characteristics of reactions of this type. This also applies to decarboxylation reactions coupled with oxidation[20], i.e. to the reaction involving the oxidation of the hydrocarbon group of the acid, which is accompanied by decarboxylation.

II. THERMAL OXIDATIVE DECARBOXYLATION UNDER THE INFLUENCE OF TRANSITION METAL SALTS AND PERSULPHATES

The reactions of carboxylic acids with transition metal salts have been studied as a rule in water, acetonitrile, benzene, and the carboxylic acids themselves. The formation of the metal carboxylates constitutes a rapid pre-equilibrium stage of the decarboxylation reaction in carboxylic acids and in benzene in the presence of metal salts:

$$\mathrm{M(OAc)}_n + n\,\mathrm{RCO_2H} \rightleftarrows \mathrm{M(O_2CR)}_n + n\,\mathrm{HOAc} \ .$$

Metal carboxylates have been studied in detail by various physicochemical methods. Investigation of infrared and ultraviolet (220–270 nm) absorption spectra of lead carboxylates made it possible to classify them as charge-transfer complexes[21]. Solutions of cerium(IV) acetate in carboxylic acids have a yellow orange colour[22] and are stable for several days when kept in the dark in the absence of water and air. The cerium complex of acetic acid in aqueous solutions has an absorption band with a maximum at 286 nm.[23] Monomeric, dimeric, and trimeric cerium complexes of acetic acid have been detected spectrophotometrically[24]. Thallium(III) valerate in cyclohexane has a broad absorption band in the near ultraviolet below 360 nm.[25] Studies of the mass spectra of thallium(III) carboxylates led to the detection of the ions $(CH_3CO_2)_3Tl^+$ and $(C_6H_5CO_2)_nTl^+$, where $n = 1$ or 2.[26] In cobalt(III) acetate, which exists in a dimeric form in acetic acid, the acetoxy-groups are easily substituted by the anions of butyric, isobutyric, and pivalic acids[27]. Apparently one cannot always expect the complete substitution of the acetoxy-groups in metal acetates by the carboxylate groups of higher acids—incomplete substitution has been observed in the reaction of manganese(III) acetate with pivalic acid[28]:

$$\mathrm{Mn(OAc)_3} + \mathrm{RCO_2H} \rightleftarrows \mathrm{Mn(OAc)}_{3-n}\mathrm{(O_2CR)}_n + n\,\mathrm{HOAc} \ .$$

In an aqueous medium the Ce^{4+} [23] and Co^{3+} [14] cations interact with the undissociated forms of the acids:

$$\mathrm{Ce(H_2O)_8^{4+}} + \mathrm{RCO_2H} \rightleftarrows \mathrm{[Ce(H_2O)_7\,RCO_2]^{3+}} + \mathrm{H^+} + \mathrm{H_2O} \ ;$$

$$\mathrm{Co(H_2O)_6^{3+}} + \mathrm{RCO_2H} \rightleftarrows \mathrm{[Co(H_2O)_5\,RCO_2]^{2+}} + \mathrm{H^+} + \mathrm{H_2O} \ .$$

The decomposition of metal carboxylates, accompanied by decarboxylation, can occur on heating; we have called this process thermal oxidative decarboxylation. The yield and composition of the products of this reaction depend on the structure of the acid. Literature data are therefore considered below for different types of carboxylic acids.

1. Alkane- and Arylalkane- Carboxylic Acids

Thermal oxidative decarboxylation of alkane- and arylalkane-carboxylic acids yields alkanes, alkenes, esters, and other products, the yield of which depends significantly on the structure of the carboxylic acid RCOOH. For the same oxidant, the yield of alkenes and esters decreases in the following sequence of groups R: tertiary > secondary > primary. This sequence is correlated with the increase of the ionisation potentials of the radicals and with the decrease of the stability of the carbonium ions[16].

The yield and composition of the decarboxylation products also depend significantly on the kind of oxidant and on the reaction mechanism, so that further consideration of the thermal oxidative decarboxylation in this Section can be usefully related to the characteristics of the reaction mechanism for the following groups of oxidants: one-electron (Ce^{4+}, Ag^{2+},

Co^{3+}, and Mn^{3+}), two-electron (Pb^{4+} and Tl^{3+}), binary systems containing Cu^{2+} (Pb^{4+}–Cu^{2+}, Mn^{3+}–Cu^{2+}, and Co^{3+}–Cu^{2+}), and persulphates.

(a) *One-electron oxidants.* The equations of the decarboxylation reactions under the influence of Co^{2+},[27] Mn^{3+},[28] Ce^{4+},[29] and Ag^{2+},[30] in which mainly the products of one-electron and two-electron oxidation are formed, are as follows:

$$M^n(O_2CCH_2CH_2CH_3)_n \rightarrow M^{n-1}(O_2CCH_2CH_2CH_3)_{n-1} + CH_3CH_2CH_3 + CO_2 ,$$

$$2M^n[O_2CC(CH_3)_3]_n \rightarrow 2M^{n-1}[O_2CC(CH_3)_3]_{n+1} + (CH_3)_2C{=}CH_2 + CO_2 + (CH_3)_3CCOOH .$$

It is interesting to consider how the composition of the thermal oxidative decarboxylation varies with the type of metal ion. A clear-cut dependence of the yield of the decarboxylation products on the normal reduction potentials of the metal ions was not observed[16]. Thus the reduction potential of Cu^{2+} (0.153 eV) is much lower than that of Co^{3+} (1.84 eV), Ag^{2+} (2.0 eV), Ce^{4+} (1.70 eV), and Mn^{3+} (1.51 eV), but the yield of the total oxidation products (alkenes and esters) is greater when the reaction is carried out in the presence of Cu^{2+}.[15,16,31]

It follows from a series of data[27–30] that the dependence of the ratio of the yield of total oxidation products to the yield of one-electron oxidation products (alkanes) on the type of oxidant is different for acids of different structure. For butyric acid, the ratio varies in the sequence $Ag^{2+} > Ce^{4+} > Mn^{3+} > Co^{3+}$, for isobutyric acid the sequence is $Ce^{4+} > Ag^{2+} > Mn^{3+} > Co^{3+}$, and for pivalic acid the sequence is $Ag^{2+} \cong Co^{3+} > Mn^{3+} > Ce^{4+}$. However, the data presented above were taken from several investigations in which the reaction conditions were not identical, so that it is extremely difficult to reach reliable conclusions concerning the dependence of the yield of the reaction products on the type of oxidant. The yield and composition of the reaction products apparently depends to a much greater extent on the decarboxylation mechanism than on the reduction potential of the metal ion.

Kinetic studies have shown[23] that the rate-limiting stage in the decarboxylation of acetic acid on treatment with Ce^{4+} in an aqueous medium is the decomposition of the complex:

$$[Ce(H_2O)_7OAc]^{3+} \rightarrow [Ce(H_2O)_6]^{3+} + H_2O + OAc^{\cdot}$$

Further decomposition of the acetoxy-radical to the methyl radical leads to the formation of methane as the main product. The reaction is faster in the water–acetonitrile mixture than in pure water.

The kinetics of the oxidative decarboxylation by Ce^{4+} of alkane- and arylalkane-carboxylic acids have been studied in an aqueous medium[32–37] and Ag^{2+}.[38] The rate of reaction is described by a second-order kinetic equation (first order with respect to the oxidant and first order with respect to carboxylic acid). The reaction is catalysed by added Ag^{+} and H^{+} ions. According to the authors, the adduct of an acid molecule and Ag^{+} is initially formed reversibly and then decomposes under the influence of Ce^{4+} with formation of the acyloxy-radicals $RCOO^{\cdot}$. The rate of reaction is limited by the stage involving the decomposition of the complex; this has received additional confirmation by the fact that the equilibrium constants of the process involving the formation of the Ce^{4+}–alcohol complex are insensitive to electronic effects[39], while the rate of decarboxylation depends significantly on the type of substituent. This is seen from the following data[23] {50°, $I = 1,2$, $[H^{+}] = 1M$}:

Carboxylic acid	Isobutyric	Propionic	Acetic	Chloroacetic
$10^4 k_2$, litre mol^{-1} s^{-1}	17.5	3.25	1.25	0.71

The logarithms of the relative rate constants for the decarboxylation of substituted phenylacetic acids in aqueous acetonitrile are correlated with the σ^{+} constants of the substituents[40]. The quantity $\rho = -2.93 \pm 0.48$ obtained indicates a polar structure of the transition state:

$$ArCH_2COOH + Ce^{4+} \rightarrow ArCH_2\overset{O}{\underset{O}{\diagdown\!\diagup}}Ce^{4+} \rightarrow ArCH_2^{\cdot} + CO_2 + Ce^{3+} + H^{+} .$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad H$$

The formation of benzyl radicals in this reaction is indicated by the increased yield of benzaldehyde in the presence of oxygen.

It has been suggested[23] that the mechanism of the oxidation of carboxylic acids on treatment with Ce^{4+} is of the inner-sphere type. An analogous mechanism has been attributed to the reaction of carboxylic acids with Co^{3+} salts, in which the formation of benzyl radicals has been confirmed by the detection of bibenzyl in the reaction products (1%).[14] The formation of intermediate radicals in the oxidation of ω-phenylalkanecarboxylic acids by cobalt salts in aqueous acetone solutions was demonstrated using bromoform as a trapping agent and identifying the alkyl bromides obtained[41]. The rate of decarboxylation of aliphatic acids under the influence of Co^{3+} varies in the following sequence[14]:

$$CH_3COOH < CH_3CH_2COOH < (CH_3)_2CHCOOH < (CH_3)_3CCOOH .$$

In this sequence the activation energy decreases by 4 kcal mol^{-1} on replacement of the α-hydrogen atom by the methyl group. Since the inductive influence of the CH_3 group on the homolysis of the O–Co bond via the R–COO system should be weak, there is a possibility of a two-stage decomposition of the complex with the preliminary formation of an acyloxy-radical. However, since the stability of the radicals increases in the sequence $CH_3 < C_2H_5 <$ iso-$C_3H_7 <$ t-C_4H_9, the authors[14] believe that a synchronous mechanism for the decomposition of cobalt carboxylates is more likely[14].

The appreciable dependence of the rate of reaction on the nature of the alkyl groups in the carboxylic acid in accordance with the sequence pivalic acid > isobutyric acid > butyric acid under the influence of Co^{3+},[14,27] Mn^{3+},[28] or Ag^{2+}[38] leads to the conclusion that the formation of alkyl radicals $R^{\cdot}$ involves a synchronous mechanism. On the other hand, the small difference between the rates of decarboxylation of acids of different structure under the influence of Ce^{4+} [23,29] indicates the formation of acyloxy-radicals $RCOO^{\cdot}$.

The study of the kinetics of the decarboxylation of carboxylic acids by Co^{3+} [27] and Mn^{3+} [28] in solutions in the carboxylic acids themselves showed that the power exponent of the concentration of the corresponding metal carboxylate in the kinetic equation for the reaction is unity. The activation energy for the oxidation of pivalic acid by cobalt salts at 61–100 °C is 30 kcal mol^{-1}, while under the influence of manganese salts in the presence of 3.5M acetic acid the activation energy is 34.6 kcal mol^{-1}. These values are close to the energies of the decomposition of the carboxylates, which are less than 40 kcal mol^{-1}. The rate constant for the oxidation of pivalic acid by Mn^{3+} ($\sim 4.5 \times 10^{-4}$ s^{-1}, 70 °C) is higher than the rate constant for the analogous reaction with Co^{3+} ($\sim 0.8 \times 10^{-4}$ s^{-1}, 71 °C). For these two oxidants, different yields of products are also observed. On passing from Mn^{3+} to Co^{3+}, the ratio of the yield of the total oxidation products (alkenes, esters) to the yield of the one-electron oxidation products (alkanes) changes from 0.3 to 0.2 in the decarboxylation of butyric acids and from 0.5 to 0.3 in the decarboxylation of isobutyric acid. The increase of the yield of alkenes and esters is probably associated with the fact that the rate of oxidation of the radicals to carbonium ions by Mn^{3+} is greater than the rate of oxidation by Co^{3+}.

The concentration of protons in solution has a significant influence on the rate of decarboxylation and the yield of reaction products. The rate of decarboxylation of acetic acid by Ce^{4+} in an aqueous medium increases with increase in proton concentration, apparently as a consequence of the increase of the redox potential of the Ce^{4+}–Ce^{3+} system, which indicates a greater activity of the non-hydrolysed complexes[23]:

$$[Ce(H_2O)_7OH]^{3+} + H^+ \rightleftharpoons [Ce(H_2O)_8]^{4+} \quad .$$

In the reaction of carboxylic acids with Co^{3+} in water the hydrolysed complex having the composition $[Co(H_2O)_5(OH)]^{2+}$ interacts with acids more readily than the unhydrolysed complex, so that, with increase of the $HClO_4$ concentration, the rate of decarboxylation diminishes[14]. However, when carboxylic acids themselves are used as solvents, the carboxylation under the influence of all metals (Mn^{3+},[28] Co^{3+},[27] and Ce^{4+} [29]) is catalysed by added strong acids ($HClO_4$ and ClCCOOH). Under these conditions, the yield of alkenes and esters as a rule increases. It has been suggested that this is associated with the formation of a positively charged complex:

$$Ce(O_2CR)_4 + H^+ \rightleftharpoons [Ce(O_2CR)_3]^+ + RCOOH \quad .$$

which, being coordination unsaturated, undergoes oxidation-reduction decomposition with greater ease than the corresponding neutral complex[29]:

$$[Ce^{IV}(O_2CR)_3]^+ \rightarrow [Ce^{III}(O_2CR)_2]^+ + RCOO^{\cdot} \text{ etc.}$$

It is of interest to note that the hydrocarbon chain oxidation reactions compete with the decarboxylation of phenylacetic acids[14,42]:

$$PhCH_2COOH \begin{cases} \longrightarrow PhCH_2^{\cdot} + CO_2 \\ \longrightarrow PhC^{\cdot}HCOOH \end{cases} .$$

The H–C bond is oxidised fairly readily in the interaction of formic acid with Ag^{2+},[43] Mn^{3+},[44] Tl^{3+},[45] and Hg^{2+}.[46]

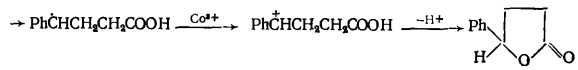
On the basis of the high value of ρ, atypical for a free-radical process, and the observation of EPR signals due to radical-cations, Dessau and Heiba[42] suggested that the oxidative decarboxylation of arylacetic acids by cobalt acetate in an aqueous medium includes a stage involving the one-electron oxidation of the benzene ring. A similar value of ρ, equal to −2.91, was obtained in the oxidative decarboxylation of substituted phenylacetic acids by cerium ammonium nitrate in 30% aqueous acetonitrile[40]. The intermediate formation of a radical-cation was observed also in the electrochemical oxidation of salts of methoxyphenylacetic acid[47–49].

One should note that, whereas the formation of free radicals in the first decarboxylation stage in aqueous solutions has been demonstrated fairly convincingly, their subsequent oxidation to carbonium ions has been studied to a much smaller extent. This is apparently due to the difficulty of the quantitative isolation and identification of the products in an aqueous medium and also to the possibility of secondary processes involving the oxidation of the products obtained from the radicals. The most convincing evidence for the intermediate formation of carbonium ions in the oxidation of arylacetic acids by cobalt salts in acetic acid is high (50 to 100%) yields of phenylacetates[42]:

$$PhCH_2COOH \xrightarrow[-Co^{2+}]{Co^{3+}} (PhCH_2COOH)^{+} \xrightarrow[-H^+]{-CO_2} PhCH_2^{\cdot} \xrightarrow[-Co^{2+}]{Co^{3+}} PhCH_2^{+} \xrightarrow{OAc^-} PhOAc \; .$$

The radical-cation mechanism of the decarboxylation of arenecarboxylic acids by cobalt salts is also supported by the formation of γ-phenylbutyrolactone (yield >25%) when γ-phenylbutyric acid interacts with cobalt acetate:

$$PhCH_2CH_2CH_2COOH \xrightarrow{Co^{3+}} (PhCH_2CH_2CH_2COOH)^{+} \xrightarrow{-H^+} \rightarrow PhCHCH_2CH_2COOH \xrightarrow{Co^{3+}} PhCHCH_2CH_2COOH \xrightarrow{-H^+}$$

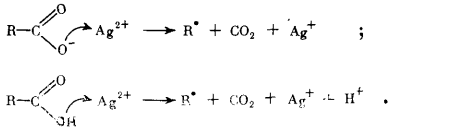


It has been suggested[29] that the oxidation of the radicals in the oxidative decarboxylation of carboxylic acids by Ce^{4+} takes place via an inner-sphere mechanism involving the formation of an alkylcerium intermediate. The latter is converted into Ce^{3+} and a carbonium ion, from which alkenes and esters are formed:

$$R^{\cdot} + Ce^{4+} \rightleftharpoons [RCe]^{4+} \rightarrow Ce^{3+} + R^+ \quad .$$

The mechanism of the oxidation of alkyl radicals by other one-electron oxidants, such as Cu^{2+}, Co^{3+}, and Mn^{3+}, is similar to the mechanism of the oxidation by Ce^{4+}.[16]

The problem of whether or not metal ions interact with undissociated acid molecules or with carboxylate ions is more complex. The rate of reaction of Ce^{4+} with formic acid is proportional to the $HClO_4$ concentration, which is attributed to the presence of the complexes $Ce^{4+}.HCOOH$ and $Ce^{4+}.HCOO^-$. It is assumed that the reaction proceeds almost exclusively with participation of the complex $Ce^{4+}.HCOO$.[50] It is believed that[38] the interaction of Ag^{2+} with carboxylic acids in an aqueous acid medium takes place with participation of both species—RCOOH and $RCOO^-$:



(b) *The two-electron oxidants Pb^{4+} and Tl^{3+}.* Two reviews have been devoted to the oxidative decarboxylation of carboxylic acids by lead tetra-acetate[16,51]. The reactions of alkane- and arylalkane-carboxylic acids with $Pb(OAc)_4$ yield mainly alkanes, alkenes, and esters, the yield of which depends on the structure of the acid. The relative rates of decarboxylation of the acids RCOOH by lead tetra-acetate decrease as a function of R in the following sequence: tertiary > secondary > primary. The yield of alkenes and esters decreases and the amount of alkanes increases in the same sequence. The stoichiometric equations for the decarboxylation of pivalic[52] and formic[53] acids by lead tetra-acetate show that the oxidant is of the two-electron type:

$$Pb(O_2CR)_4 \begin{cases} \longrightarrow Pb(O_2CR)_2 + RCO_2R + CO_2 \\ \longrightarrow Pb(O_2CR)_2 + R(-H) + RCO_2H + CO_2 \end{cases} ;$$

$$Pb(O_2CH)_4 \rightarrow Pb(O_2CH)_2 + HCOOH + CO_2 \quad ; \quad R = C(CH_3)_3 \quad .$$

It was assumed initially[53,54] that the reaction mechanism includes the heterolytic splitting of lead tetracarboxylates with formation of lead dicarboxylate and acyloxonium or carbonium ions as intermediates:

$$(RCO_2)_4Pb \rightarrow RCOO^+ + Pb(OCOR)_2 + RCOO^- \quad ,$$
$$(RCO_2)_4Pb \rightarrow R^+ + CO_2 + Pb(OCOR)_2 + RCOO^- \quad .$$

However, subsequently Kochi's work showed[15,52] that the decarboxylation of carboxylic acids by $Pb(OAc)_4$ is inhibited by oxygen and accelerated by radical reaction initiators, proceeding as a chain process via the following mechanism:

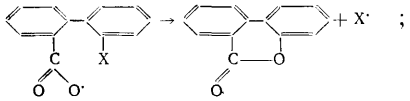
$Pb(OCOR)_4 \rightarrow Pb(OCOR)_3 + CO_2 + R^{\cdot}$ (initiation stage);
$Pb(OCOR)_3 \rightarrow Pb(OCOR)_2 + CO_2 + R^{\cdot}$ (chain propagation);
$Pb(OCOR)_4 + R^{\cdot} \rightarrow Pb(OCOR)_3 +$ alkene, ester;
$Pb(OCOR)_3 + R^{\cdot} \rightarrow Pb(OCOR)_2 +$ alkene, ester (chain termination);
$R^{\cdot} + SH$ (solvent) $\rightarrow RH + S^{\cdot}$
$R^{\cdot} + R^{\cdot} \rightarrow$ dimers, disproportionation products.

The decarboxylation of carboxylic acids by $Pb(OAc)_4$ begins, as in the case of other oxidants, with the pre-equilibrium formation of lead carboxylates[15,21]:

$$Pb(OAc)_4 + n\,RCO_2H \rightleftharpoons Pb(OAc)_{4-n}(O_2CR)_n + n\,HOAc \quad .$$

In the presence of pyridine, which accelerates decarboxylation, the pre-equilibrium complex has the form $Pb^{IV}(O_2Cr)_n \cdot Py_m$. The reactions are promoted also by the addition of other nitrogen bases (triethylamine) as well as salts (acetates).

Lead carboxylates decompose with formation of Pb^{3+} and RCOO· or R·. The intermediate formation of carboxy-radicals was detected in certain cases from the yield of the corresponding products. When 2'-substituted biphenyl-2-carboxylic acids interact with lead tetra-acetate in boiling benzene under a nitrogen atmosphere, 3,4-benzocoumarin is formed in a high yield[55]:



X=H, CO_2H, Cl, NO_2, OCH_3, or CO_2CH_3 .

The formation of alkyl radicals was confirmed by EPR in the photolysis of lead carboxylates at low temperatures[21,56]. No evidence was obtained for the formation of Pb^{3+} by EPR,[57] but its formation is indicated by the results of kinetic studies of the oxidation of Co^{2+} and Ce^{3+} by lead tetra-acetate. The rates of these reactions are described by a common second-order kinetic equation (first-order with respect to each reactant), which suggests the intermediate formation of Pb^{3+} as a result of one-electron transfer in the rate-limiting stage of the reaction[58].

The involvement of alkyl radicals in a number of reactions has been demonstrated with the aid of spin-trapping agents, for which nitroso-compounds are used[59]:

$$R'NO + R\cdot \rightarrow R'\underset{\displaystyle O\cdot}{\underset{|}{N}}-R \quad .$$

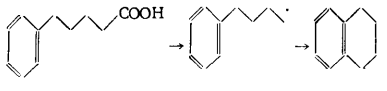
At −40 °C free radicals R' were trapped in methylene chloride as asymmetric nitroxy-radicals. At 25 °C secondary radicals, obtained as a result of the abstraction of α-hydrogen from the acid molecule, were trapped:

$$R\cdot + R''CH_2COOH \rightarrow R''\dot{C}HCOOH \xrightarrow{R'NO} R''-\underset{\displaystyle \cdot O}{\underset{|}{N}}-\underset{\displaystyle COOH}{\underset{|}{CH}}-R' \quad .$$

In the presence of oxygen alkyl radicals can give rise to side products[15]:

$$CH_3CH_2\dot{C}HCH_3 + O_2 \rightarrow CH_3CH_2\underset{\displaystyle O_2\cdot}{\underset{|}{C}}HCH_3 \rightarrow CH_3CH_2COCH_3 + CH_3CH_2CHOHCH_3 \quad .$$

In certain cases the intermediate radicals are converted into cyclic reaction products. The cyclisation of alkyl radicals in the decarboxylation of ethyl 2-carboxy-5-phenylvalerate by lead tetra-acetate leads to the formation of tetralincarboxylate derivatives[60]. The oxidative decarboxylation by lead tetra-acetate of 5-phenylvaleric acid in benzene solution in a nitrogen atmosphere yields tetralin as the main product[61]:



A similar reaction takes place with *p*-nitro- and *p*-methoxy-derivatives of phenylvaleric acid and also with 5-(*p*-methoxyphenyl)-5-phenylvaleric and 5-(β-naphthyl)valeric acids[62]. The oxidation of *o*-benzoylbenzoic acid by lead tetra-acetate in benzene leads to benzophenone, *o*-phenylbenzophenone, and fluorenone[63].

Thus the process is undoubtedly of a radical type. The question arises of the pathways whereby alkenes and esters are obtained in the reaction. These pathways can include further oxidation of the radicals to carbonium ions as a result of electron transfer [reaction (4)] or oxidative heterolysis [reaction (5)] of the organolead compound $RPb(OCOR)_3$, which is formed either via a reaction of the S_N2 type or by the interaction of the radical with $Pb(OCOR)_3$:

$$R\cdot + Pb(OCOR)_4 \rightarrow R^+ + Pb(OCOR)_3^- + RCO_2^- \quad ; \qquad (4)$$

$$R\cdot + Pb(OCOR)_4 \rightarrow RPb(OCOR)_3 + R\cdot + CO_2 \quad ;$$

$$R\cdot + Pb(OCOR)_3 \rightarrow RPb(OCOR)_3 \quad ;$$

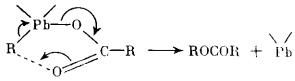
$$RPb(OCOR)_3 \rightarrow R^+ + Pb(OCOR)_2 + RCO_2^- \quad . \qquad (5)$$

The organolead compound can be converted into alkenes and esters without the intermediate formation of carbonium ions, as a result of the elimination [reaction (6)] or reactions (7) of the S_N2 type:

$$-\underset{|}{\overset{H}{\underset{|}{C}}}-\underset{|}{C}-Pb(OCOR)_3 \rightarrow \rangle C{=}C\langle + Pb(OCOR)_2 + RCOOH \quad ; \qquad (6)$$

$$RCO_2^- + RPb(OCOR)_3 \rightarrow RCOOR + Pb(OCOR)_2 + RCO_2^- \quad . \qquad (7)$$

The possibility of the formation of esters directly in the decomposition of lead carboxylates via an intramolecular S_Ni mechanism (not only cations but also radicals should then be formed as intermediates) has also been suggested[66]. However, this mechanism (ligand transfer) is more likely for the decomposition of the organolead compound[65]:



(8)

Tertiary alkyl radicals are readily oxidised by lead tetra-acetate; on the other hand, primary radicals are oxidised with difficulty, as a result of which the decarboxylation under the influence of $Pb(OCOCH_3)_4$ leads mainly to the formation of alkanes. A thermodynamic assessment of the reactions[64] agrees with these results. The electrode potential of the Pb^{2+}/Pb^{4+} system ($E^0 = 1.69$ V) is not sufficiently high for the oxidation of primary radicals ($E^0 = 2.07$ V for the $C_2H_5/C_2H_5^+$ system) but is sufficient for the oxidation of secondary and tertiary radicals ($E^0 = 1.59$ V for iso-$Pr^{\cdot}$/iso-Pr^+ and $E^0 = 1.27$ V for t-Bu·/t-Bu) as well as allyl ($E^0 = 1.7$ V) and benzyl ($E^0 \cong 1.5$ V) radicals.

The electrode potential for the two-electron process $C_2H_5 \cdot COO^- \rightarrow R^+ + CO_2 + 2e^-$, equal to 1.68 V, is close to the potential for the Pb^{2+}/Pb^{4+} system, which accounts for the formation of esters from primary carboxylic acids.

It is of interest that, on decarboxylation of crystalline α-isobutyric acid by lead tetra-acetate at low temperatures, even tertiary radicals are not oxidised to carbonium ions and are converted quantitatively into alkanes[21].

The oxidation of primary alkyl radicals can proceed effectively via the ligand transfer mechanism. The decarboxylation of carboxylic acids under the influence of lead tetra-acetate in the presence of LiCl or LiBr results in almost quantitative formation of alkyl halides[67]. The reaction is important for the synthesis of alkyl chlorides, but it also proceeds with bromides and iodides. The optimum conditions require one equivalent of LiCl per equivalent of $Pb(OCOCH_3)_4$. The yield of alkyl halides obtained by this method decreases in the sequence of acids RCOOH as a function of the nature of R: tertiary > secondary > primary.

The 1.37–1.43 : 1 ratio of *erythro*- and *threo*-2-chloro-3-phenylbutanes in the halogenodecarboxylation of *erythro*- and *threo*-2-methyl-3-phenylbutyric acids indicates a radical mechanism of this process, since, on treatment of these acids with lead tetra-acetate, the *erythro*- and *threo*-acetates are formed via an ionic mechanism in equal amounts[68]. Furthermore, the halogenodecarboxylation is strongly inhibited by oxygen. On this basis, the following radical mechanism has been proposed for the halogenodecarboxylation reaction:

Pre-equilibrium stage:

$$Pb^{IV}(O_2CR)_4 + X^- \rightleftharpoons [(RCO_2)_4 Pb^{IV}X]^- \ .$$

Initiation stage:

$$[(RCO_2)_4 Pb^{IV}X]^- \rightarrow R^\cdot + CO_2 + [(RCO_2)_3 Pb^{III}X]^- \ ;$$
$$[(RCO_2)_4 Pb^{IV}X]^- \rightarrow X^\cdot + [(RCO_2)_4 Pb^{III}]^- \ .$$

Chain propagation:

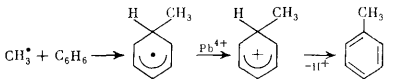
$$R^\cdot + [(RCO_2)_4 Pb^{IV}X]^- \rightarrow RX + [(RCO_2)_4 Pb^{III}]^- \text{ (ligand transfer);}$$
$$X^\cdot + [(RCO_2)_4 Pb^{IV}X]^- \rightarrow X_2 + [(RCO_2)_4 Pb^{III}]^- \ ;$$
$$[(RCO_2)_4 Pb^{III}]^- \rightarrow R^\cdot + CO_2 + [(RCO_2)_3 Pb^{II}]^- \ ;$$
$$R^\cdot + X_2 \rightarrow RX + X^\cdot, \text{ etc.}$$

Chain termination:

$$R^\cdot + [(RCO_2)_3 Pb^{III}X]^- \rightarrow RX + [(RCO_2)_3 Pb^{II}]^- \ .$$

The halide formation reaction proceeds via the ligand transfer mechanism. This is indicated particularly by the finding that the halogenodecarboxylation of cyclobutanecarboxylic and β,β-dimethylbutyric acids proceeds without a rearrangement and is accompanied by the formation of cyclobutyl chloride and neopentyl chloride[67]. It has been shown[69] that the ligand transfer reaction in the decarboxylation of phenylacetic acid and its substituted derivatives (R = *p*-NO_2 or *p*-Cl) is little influenced by the polarity of the substituent, while in the absence of LiCl both the products and the rate of reaction depend greatly on the substituents.

The oxidative decarboxylation of tertiary acids by lead tetra-acetate has been studied in relation to t-butylperoxy-2-methylpropanoic acid in benzene[70]. The mechanism of the formation of toluene proposed in the above study, according to which the active methyl radical obtained in the decomposition of the t-butoxy-radical adds to benzene and the subsequent oxidation of this product and the elimination of a proton lead to toluene, is of interest:



The decarboxylation of 2,3,3-trimethylbutyric acid by lead tetra-acetate in benzene and acetic acid yields mainly 3,3-dimethyl-2-butyl acetate and, when Cu^{2+} is involved in the reaction, the main product is 3,3-dimethylbut-1-ene.[65] The low yield of rearranged products in both cases suggests that ionic intermediates are not formed in the reaction. Organocopper and organolead compounds are apparently formed as intermediates in the reaction and decompose as a result of β-elimination with formation of alkenes [Eqn.(6)] or intramolecular substitution (ligand transfer mechanism or S_Ni mechanism) with formation of acetates.

The decarboxylation of carboxylic acids[25] in benzene by Tl^{3+} is much slower than under the influence of Pb^{4+}. All types of acids give rise to a large amount of radical products and a small amount of esters, which is due to the low reduction potential of the Tl^{3+}/Tl^{+} pair ($E^0 = 1.25$ V) and $Tl^{3+} + Cl^-/TlCl$ ($E^0 = 1.36$ V). The yield of esters decreases in the following sequence for acids RCOOH with different R: $C_6H_5.CH_2$ (~20%) > tertiary (10–20%) > secondary > primary. This process is not greatly promoted by the addition of acetate salts and pyridine. However, the reaction is appreciably accelerated when it is carried out using carboxylic acids as solvents. The addition of strong acids ($HClO_4$, BF_3, $CF_3.COOH$) increases the rate of reaction still further. Under these conditions, the decarboxylation of isobutyric and butyric acid yields mainly esters and small amounts of alkanes and alkenes. The stoichiometric reaction equation obtained in this case indicates a two-electron mechanism of this process:

$$(RCO_2)_3 Tl^{III} \rightarrow \begin{cases} \rightarrow R{-}R + 2CO_2 + Tl^{I}O_2CR \\ \rightarrow R(-H) + CO_2 + RCO_2H + Tl^{I}OCOR \\ \rightarrow RCO_2R + CO_2 + Tl^{I}OCOR \end{cases} .$$

(c) *Binary systems containing* Cu^{2+}. The oxidative decarboxylation of carboxylic acids by the binary systems Mn^{3+}–Cu^{2+},[28] Co^{3+}–Cu^{2+},[27] Ag^{2+}–Cu^{2+},[30] and Pb^{4+}–Cu^{2+} [31] leads to an appreciable increase of the yield of alkenes. In the presence of catalytic amounts of copper salts the rate of decarboxylation increases appreciably and the reaction becomes of preparative importance for the synthesis of alkenes[31,52]. This type of effect has been explained by the marked ability of copper ions to trap and oxidise intermediate alkyl radicals. The rate constants for the oxidation of primary and secondary alkyl radicals by copper salts are 10^6–10^9 litre mol^{-1} s^{-1},[69,71,72] which indicates the following mechanism of the formation of alkenes:

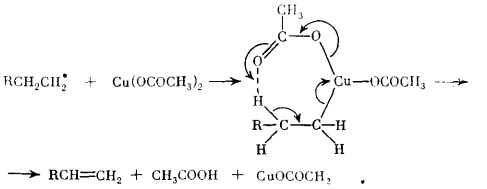
$$R^\cdot + Cu^{2+} \rightarrow R(-H) + Cu^{+} \ .$$

Under these conditions, the copper(I) ion is oxidised by lead tetra-acetate, propagating the chain:

$$Pb^{IV}(OCOR)_4 + Cu^{I}OCOR \rightarrow Pb^{III}(OCOR)_3 + Cu^{II}(OCOR)_2 \text{ etc.}$$

Torssell[64] believes that the low oxidation-potential of the Cu^{+}/Cu^{2+} (0.17 V) and $CuCl/Cu^{2+} + Cl^-$ (0.57 V) systems is inconsistent with this mechanism. However, since a large amount of alkenes and a small amount of esters, coupling products, and alkanes are formed in the oxidation of carboxylic acids in the presence of copper ions, the β-elimination mechanism has been proposed. The process $C_2H_5COO^- \rightarrow C_2H_4 + CO_2 + H^+ + 2e$ is characterised by the quantity $E^0 = 0.31$ V. $E^0 = 0.64$ V has been calculated for the $C_2H_5^\cdot \rightarrow C_2H_4 + H^+ + e$ system. These data suggested that the specific oxidising effect of copper ions involves simultaneous action on the β-hydrogen and the unpaired electron. Radicals without β-hydrogen should not then be actively oxidised by copper ions. Indeed the products and rate of decarboxylation of phenylacetic acid by lead tetra-acetate with and without added Cu^{2+} differ little. The weak influence of added copper salts on the decarboxylation of RCOOH with a tertiary substituent R on treatment with lead tetra-acetate is probably associated with this factor[57].

It has been suggested[73] that, when the copper ion interacts with a radical, an organocopper compound is formed, its β-elimination via a cyclic transiton state leading to a multiple bond:

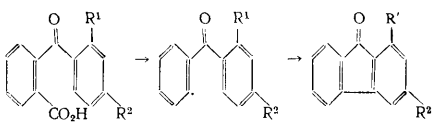


(d) *Persulphates.* The decarboxylation of aliphatic acids and their salts by sodium persulphate was studied initially by Fichter and coworkers in a series of investigations[74-77]. The reaction products are alcohols and olefins with an admixture of aldehydes and saturated hydrocarbons.

Decarboxylation in alkaline and acid media leads to products having different compositions. When acetic acid was oxidised with sodium persulphate in acid media, methane and succinic acid, which can be obtained from the intermediate free radicals, were detected in addition to CO_2 and CO. In alkaline media further-oxidation products (methanol and ethylene) were found in addition to methane and succinic acid. The oxidation of sodium acetate in the presence of sodium carbonate yielded methanol. Under the same conditions, sodium propionate yields ethanol and ethylene, the oxidation of sodium butyrate leads to the formation of propene, while isobutene and isobutyl isovalerate are obtained from the salt of isovaleric acid[75]. Such variation of the composition of the products with increase of chain length and with branching of the alkyl residue is apparently associated with the facilitation of the oxidation of the intermediate radicals R· and with the increase of the stability of the intermediate carbonium ions formed under these conditions.

The formation of radicals in the oxidation of phenylacetic acid and a number of related acids in an aqueous medium on treatment with the $Na_2S_2O_8$–Tl^{3+} system has been demonstrated by EPR.[78] The formation of aryl radicals in the decarboxylation of benzoic, phenylacetic, and diphenylacetic acids with $Na_2S_2O_8$ has been confirmed by the isolation of the products by the dimerisation of the corresponding radicals—biphenyl, 1,2-diphenylethane, and 1,1,2,2-tetraphenylethane[79]. In the presence of pyridine the oxidation of benzoic acid results in the formation of approximately 5% of phenylpyridines.

The cyclisation of the intermediate radicals on decarboxylation of substituted *o*-benzoylbenzoic acids yielded substituted fluorenones[79]:



R^1=H, R^2=H, Cl, Br, CH_3, or OCH_3; R^1=R^2=OCH_3, or CH_3.

Active oxidising agents arise in the homolytic decomposition of persulphate ions on heating. The energy of this reaction is approximately 30 kcal mol^{-1} [80]:

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot-} \ .$$

Further reactions of the radical-anion in an aqueous medium in the presence of a carboxylic acid are described by the following equations[79,81]:

$$SO_4^{\cdot-} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HSO_4^- + OH^\cdot \ ;$$

$$SO_4^{\cdot-} \text{ (or } {}^\cdot OH) + RCO_2^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} SO_4^{2-} \text{ (or } {}^-OH) + RCOO^\cdot \longrightarrow \underset{\text{products}}{} R^\cdot + CO_2 \ .$$

This reaction mechanism has been confirmed by the composition of the products and by the form of the kinetic equation[81]:

$$\frac{d[CO_2]}{dt} = \frac{d[RCO_2^-]}{dt} = k_3[SO_4^{\cdot-}][RCO_2^-] \ .$$

Measurement of the relative rate constants for substituted phenylacetic acids demonstrated a correlation between the logarithms of the rate constants and σ^+ with a low value of ρ, characteristic of radical reactions:

$$\lg(k/k_0) = -0.436\,\sigma^+ + 0.06 \ (r = 0.983, \ s = 0.035) \ .$$

The rate of decarboxylation of acids by sodium persulphate increases in the presence of Ag^+ and the reaction is of first order with respect to the silver ion and peroxydisulphate and of zero order with respect to the acid[82,83]:

$$\frac{d[CO_2]}{dt} = \frac{d[S_2O_8^{2-}]}{dt} = k_2[Ag^+][S_2O_8^{2-}][RCOOH]^0 \ .$$

The mechanism of the reaction involving silver ions includes the formation of the unstable Ag^{2+} ion in the rate-limiting stage, which rapidly reacts with the carboxylic acid:

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^{2-} + SO_4^{\cdot-} \ ;$$
$$Ag^+ + SO_4^{\cdot-} \rightarrow Ag^{2+} + SO_4^{2-} \ ;$$
$$Ag^{2+} + RCOOH \rightarrow Ag^+ + RCOO^\cdot + H^+ \ ;$$
$$RCOO^\cdot \rightarrow R^\cdot + CO_2 \ ;$$
$$R^\cdot + Ag^{2+} \rightarrow R^+ + Ag^+ \text{ etc.}$$

The intermediate radicals give rise to alkanes by reacting with the carboxylic acid or another hydrogen donor *HS*. The mechanism has been confirmed by the increased yield of alkanes on increasing the concentration of carboxylic acid. In this case the stoichiometry of the reaction corresponds to the following equation:

$$2RCOOH + S_2O_8^{2-} + 2HS \xrightarrow{Ag^+} 2RH + 2CO_2 + H^+ + 2SO_4^{2-} + S_2 \ .$$

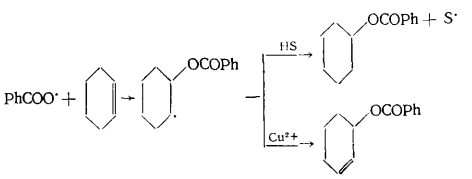
As the carboxylic acid concentration is reduced, the reaction equation becomes

$$RCOOH + S_2O_8^{2-} \xrightarrow{Ag^+} R^+ + H^+ + CO_2 + 2SO_4^{2-} \ .$$

The yield of alkanes then falls and the yield of alkenes, esters, alcohols, and further-oxidation products (ketones and aldehydes) increases.

Catalytic amounts of copper sulphate cause a sharp increase in the yield of alkenes in the decarboxylation products on treatment with the $Na_2S_2O_8$–Ag^+ system[82]. The effect of Cu^{2+} consists in the trapping and oxidation of intermediate alkyl radicals. Under these conditions, peroxydisulphate interacts with Cu^+, regenerating the initial Cu^{2+} ion. The intermediate formation of benzyl radicals in the decarboxylation of phenylacetic acids by the $Na_2S_2O_8$–Ag^+ system has been demonstrated by their reactions with substituted pyridines, which give rise to 2-benzylpyridines[83]. The alkylation of quinoline, 2-methylquinoline, isoquinoline, acridine, and substituted pyridines with the aid of a radical R· [R = CH_3, C_2H_5, $CH_3(CH_2)_2$, $CH_3(CH_2)_3$, $(CH_3)_2CH$, $(CH_2)_5CH$, or $(CH_3)_3C$], obtained by the oxidative decarboxylation of aliphatic carboxylic acids by the $Na_2S_2O_8$–Ag^+ system, has been investigated[84,85].

The oxidation of sodium benzoate and its derivatives by the $(NH_4)_2S_2O_8$–Cu^{2+} system in the presence of alkenes (cyclohexene and α-pinene)[86] leads to the formation of intermediate benzoyloxy-radicals, which add to the double bond, forming new alkyl radicals. The interaction of alkyl radicals with hydrogen donors leads to the formation of alkanes and their subsequent oxidation by Cu^{2+} ions to the corresponding cations results in the formation of alkenes and alcohols:



Intermediate phenyl radicals were detected in the decarboxylation of PhCOOH under the influence of the $Na_2S_2O_8$–Ag^+ system[87].

An extremely interesting fact is noteworthy: the decarboxylation of benzoic acids by the persulphate–Ag^+ or persulphate–Cu^{2+} system in an aqueous medium proceeds incomparably more readily than the decarboxylation under the influence of transition metal salts in non-aqueous solvents. This may be associated with the easier decarboxylation of carboxylate anions compared with undissociated molecules.

Thermal oxidative decarboxylation of alkane- and arylalkanecarboxylic acids has also been studied by a number of other workers[88-91].

2. Cycloalkanecarboxylic Acids

The decarboxylation of cycloalkanecarboxylic acids has been carried out mainly with lead tetra-acetate or its mixture with Cu^{2+}. Typical products are cycloalkanes and esters, which are believed to be formed[15,16] as a result of the intermediate involvement of carbonium ions.

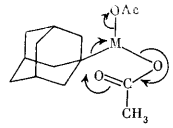
The decarboxylation of cyclopropane-[92] and cyclobutanecarboxylic acids[93] proceeds with partial ring opening and the formation of rearranged acetates, which supports the formation of ionic intermediates.

The intermediate involvement of carbonium ions is believed[54] to be indicated by the results of the decarboxylation of the optically active *endo*- and *exo*-norbornane-2-carboxylic acids by lead tetra-acetate in benzene and acetonitrile. This reaction yields almost exclusively the *exo*-acetates with an appreciable retention of optical activity. The results of the above workers[54] have been explained[94] by the fact that racemic norbornyl acetates are obtained from bridged carbonium ions, while the chiral *exo*-acetates are formed from classical carbonium ions. As a result of a skeletal rearrangement, the reaction of lead tetra-acetate with *exo*- and *endo*-bornane-2-carboxylic acids[95] yields camphene and other products as well as the *exo*- and *endo*-acetates in proportions of 68 : 32. The formation of a mixture of *exo*- and *endo*-acetates in this instance has been explained[94] by the involvement of classical and non-classical carbonium ions in the reaction.

The study of the products of the decarboxylation of bicyclo[3,2,1]octane-2-carboxylic and bicyclo[2,2,2]octane-2-carboxylic acids altered this view, showing that, apart from the pathway with participation of carbonium ions, there is a possibility also of other pathways[94]. The small difference in the proportions of the acetates obtained by the decarboxylation of *exo*- and *endo*-bicyclo[3,2,1]octane-2-carboxylic acids suggests that a radical is formed as a common intermediate: The subsequent formation of the organolead compound $RPb(OAc)_3$ and its heterolysis can lead to a non-classical carbonium ion with its subsequent conversion into an acetate. This is indicated particularly by the similar yields of the acetates in the decarboxylation and acetolysis of the corresponding tosylates[96]. However, the contribution of this reaction pathway is only 50%. Another pathway involves ligand transfer in the organolead compound via the S_Ni mechanism; this pathway is in fact responsible for the partial retention of the stereochemical configuration. In the light of these ideas, it is also possible to account for the results obtained in the decarboxylation of bornane-2-carboxylic[95] and norbornane-2-carboxylic[54] acids.

By analogy with the above data, it has been suggested that, in the decarboxylation of adamantane-2-carboxylic, adamantane-1-carboxylic, and *cis*- and *trans*-decalin-9-carboxylic acids by lead tetra-acetate in benzene in the presence of Cu^{2+} ions (or in their absence), the acetates are formed as a result of heterolysis and ligand transfer (S_Ni substitution) in the organometallic compound obtained by the interaction of the intermediate free radical with lead or copper carboxylate[65].

The high yields of acetates (89 and 93% respectively) in the decarboxylation of adamantane-1-carboxylic acid with $Pb(OAc)_4$ and $Pb(OAc)_4$–$Cu(OAc)_2$ (despite the fact that the oxidation of bridged radicals to carbonium ions should proceed with greater difficulty than the oxidation of related acyclic radicals) may indicate, according to the authors[76], a considerable contribution of the S_Ni mechanism:



M = $Pb(OAc)_2$, or Cu.

The formation of equal amounts of *cis*- and *trans*-decalinyl acetates on decarboxylation of *cis*- and *trans*-decalin-9-carboxylic acids by lead tetra-acetate and $Pb(OAc)_4$–$Cu(OAc)_2$ apparently takes place as a result of the heterolysis of organocopper and organolead compounds.

Finally, the preferred formation of the thermodynamically less stable $\Delta^{1,9}$-octalin compared with $\Delta^{9,10}$-octalin on decarboxylation of *cis*- and *trans*--decalin-9-carboxylic acids suggests, according to the authors[76], that the unsaturated cyclic compounds are obtained as a result of β-elimination from the organometallic compounds and not as a result of the deprotonation of the intermediate carbonium ion.

The products of the oxidative decarboxylation of cycloalkanecarboxylic acids have also been studied in a series of other investigations[97-103].

3. Unsaturated Carboxylic Acids

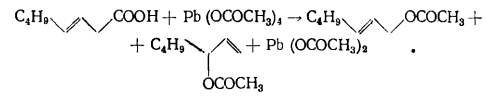
Decarboxylation of unsaturated carboxylic acids has been studied in a series of investigations[104-108]. In the decarboxylation of *trans*- and *cis*-cinnamic acids with lead tetra-acetate in benzene in an atmosphere of nitrogen, it was found unexpectedly that the main product is β-methylstyrene. It is suggested that it is formed as a result of the abstraction of the methyl radical from the intermediate complex formed by the styryl radical and lead tetra-acetate[104,107].

The general validity of this mechanism (differing from the general mechanism proposed by Kochi—see subsection 1 above) is confirmed by data obtained in the decarboxylation of a mixture of cinnamate and β-methylbutyrate salts. This reaction also leads to the formation of a radical recombination product—3-methyl-1-phenylpent-1-ene, which proved to be inactive when the optically active acid was used as the starting material. According to the authors[104], the reaction takes place as a result of the following sequence of transformations:

$$PhCH{=}CHCOOPb^{IV}OCOR \rightarrow CO_2 + [PhCH{=}CH^{\cdot} \ldots Pb^{III}OCOR] \rightarrow 2CO_2 +$$
$$+ [PhCH{=}CH^{\cdot} + R^{\cdot}] + Pb^{II} \rightarrow 2CO_2 + PhCH{=}CHR + Pb^{II} .$$

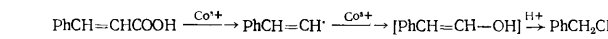
The influence of substituents in the benzene ring of cinnamic acid on the yield of products has been studied[105]. It was found that, in the presence of *p*-NO_2 and *p*-Cl substituents the main product is β-methylstyrene, as for the unsubstituted acid[104]. On the other hand, the decarboxylation of *p*-methoxycinnamic acid gives only traces of β-methylstyrene and the main products are acetates, which are believed to be formed on further oxidation of the unsaturated radical. The oxidative decarboxylation of 3-octenoic acid by lead tetra-acetate in 17% benzene solution of acetic acid leads to the formation of 3-acetoxyhept-1-ene (21%) and 1-acetoxyhept-2-ene

(30%) as the main products[69]:



The reaction is accelerated by a factor of 16 after the addition of 7% Cu^{2+}. Under these conditions, the ratio of the 3-acetoxyhept-1-ene and 1-acetoxyhept-2-ene formed is 85:15. The addition of 0.08 M pyridine increases the rates of reaction by a further factor of 5 and the ratio of the acetates changes to 55:45. The oxidative decarboxylation of vinylacetic acid by lead tetra-acetate gives rise to allyl acetate (70%) and is five times faster than the decarboxylation of 3-octenoic acid. The addition of 0.01M Cu^{2+} increases the yield of esters to 87%, but propene and hexa-1,5-diene are not formed[69]. The authors[69] suggest that the oxidation of aryl radicals by Pb^{4+} and Pb^{4+}–Cu^{2+} with participation of pyridine proceeds via a carbonium ion like the oxidation of benzyl and tertiary radicals.

The kinetics of the oxidation of unsaturated acids by cobalt perchlorate in aqueous acetonitrile in the presence of $HClO_4$ have been investigated[106]. The rate of reaction is directly proportional to the concentrations of the oxidant and the unsaturated acid and is inversely proportional to the acidity of the solution. The study of the reaction products revealed the occurrence of two simultaneous processes: oxidative decarboxylation (5–20%) and oxidation of the double bond (80–95%). The oxidative decarboxylation leads to the formation of mainly aldehydes and ketones, for example:



The main pathway—the oxidation of the double bond—results in the complete cleavage of the latter.

Acids whose double bond is conjugated with a benzene ring are oxidised more readily than acids with an unconjugated double bond. The presence of methyl or phenyl substituents at the double bond of cinnamic acid hinders oxidation. Unsaturated acids are more readily oxidised by tervalent cobalt in an aqueous medium than the corresponding saturated acids[41].

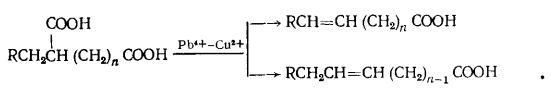
4. Dibasic Carboxylic Acids

The oxidative decarboxylation of dicarboxylic acids is usually carried out with systems containing Pb^{4+} or Pb^{4+}–Cu^{2+}. The rate of decarboxylation of alkanedicarboxylic acids having the general formula $RCH_2CH(CH_2)_nCOOH$, where



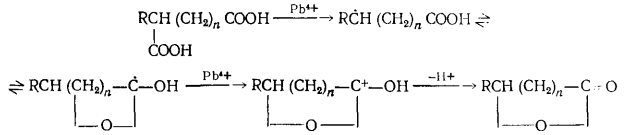
$n = 1$, 2, 3, or 10, and the composition of the reaction products depend significantly on the positions of the carboxy-groups relative to one another[109]. As the COOH groups approach one another, the decarboxylation under the influence of lead tetra-acetate slows down. The decarboxylation of the same acids by the Pb^{4+}–Cu^{2+} system proceeds equally readily for all the acids investigated. At the same time, the structure of R has virtually no influence on the decarboxylation reaction.

When equimolar amounts of the dicarboxylic acid and Pb.(OAc)$_4$ are used in the presence of copper acetate, selective decarboxylation of the carboxy-group at the secondary carbon atom takes place[109,110]. This results in a high yield of alkenoic acids in the *cis*- and *trans*-forms (in approximately equimolar amounts):



The unsaturated carboxylic acids formed can undergo further decarboxylation and conversion into alkadienes and alkenyl acetates.

The oxidation of 1,3- and 1,4-dicarboxylic acids by lead tetra-acetate yields predominantly γ- and δ-lactones[109,111]. It has been suggested that, as in the decarboxylation of monocarboxylic acids, the oxidation of dicarboxylic acids proceeds with the intermediate formation of radicals, which undergo subsequent cyclisation and oxidation:



In addition, unsaturated and saturated monocarboxylic acids are formed in this reaction.

The high yield of lactones in the decarboxylation of 2,3-diphenylglutaric and camphoric acids by lead tetra-acetate has been explained[112] by the ease of elimination of carboxy-groups at the secondary and tertiary carbon atoms respectively. The oxidative decarboxylation of glutaric acid and its monoesters (methyl, ethyl, isopropyl, and benzyl) under the influence of $Na_2S_2O_8$–Ag^+ leads to the formation of butyric acid, alkyl butyrates, and γ-butyrolactones[113]. The oxidative decarboxylation of glutaric and adipic acids by the $Na_2S_2O_8$–$AgNO_3$–$CuSO_4$ system leads to the selective formation of γ-butyrolactone and δ-valerolactone respectively[114].

When cycloalkane-1,2-dicarboxylic acids are treated with $Pb(OAc)_4$,[115-119] bisdecarboxylation takes place and results in 50–80% yields of cycloalkenes. On treatment of α,β-dicarboxylic acids with PbO_2, the yield of olefins is reduced to 25%.[120] The decarboxylation of diphenic acid under the influence of lead tetra-acetate in the acetonitrile–pyridine mixture leads to the formation of 3,4-benzocoumarin (50%); under these conditions, benzoic and phthalic acids are not decarboxylated[121].

The formation of *trans*-stilbene as the main product in the oxidative decarboxylation of *meso*- and d,*l*-1,2-diphenylsuccinic acids under the influence of Pb^{4+} [154] suggests that the bisdecarboxylation is not a synchronous β-elimination process, but includes the formation of an intermediate carbonium ion.

It has been suggested[122] that the oxidative decarboxylation of disubstituted malonic acids by lead tetra-acetate results in the formation of the diacetates $RR'C(OAc)_2$ as intermediates, whose hydrolysis leads to the ketones RR'CO. The decarboxylation of bicyclo[3,2,0]heptane-3,3-dicarboxylic acid apparently proceeds analogously, since it led to the isolation of bicyclo[3,2,0]heptan-3-one.[123]

The study of the reaction of cerium sulphate with dicarboxylic acids in sulphuric acid showed that unsaturated dicarboxylic acids (fumaric and maleic) and succinic acid are not oxidised, while phthalic, tartaric, malonic, and citric acids are oxidised on heating to 95 °C.[124] Oxalic acid readily reacts with cerium sulphate at room temperature, which makes it possible to use this reaction as an analytical method[125].

On treatment with bivalent copper, aminomalonic acid is decarboxylated with formation of glycine[126].

5. α-Hydroxyacids

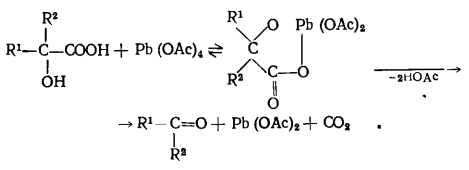
Carboxylic α-hydroxyacids contain two functional groups, which can be acted upon by oxidants. Oxidative decarboxylation of α-hydroxyacids on treatment with $Pb(OAc)_4$, first investigated by Oeda[127], obeys the stoichiometric equation

$$R_1R_2CCOOH + Pb(OAc)_4 \rightarrow R_1CR_2 + CO_2 + 2CH_3COOH + Pb(OAc)_2 \quad .$$
(OH; O)

The decarboxylation of lactic, malic, and mandelic acids[128] has been carried out with V^{5+} and that of (+)-tartaric, meso-tartaric, and dl-malic acids[129] has been carried out with Mn^{3+}. The kinetics of the oxidation of lactic, mandelic, and α-hydroxybutyric acids with participation of a series of oxidants (Cr^{6+}, Mn^{3+}, Ce^{4+}, V^{5+}) have been investigated[130]. In the presence of an excess of the acids, the rate of reaction obeys a pseudo-first-order kinetic equation (with respect to the oxidant). The kinetic isotope effect in the oxidation of mandelic and α-deuteromandelic acids by Mn^{3+} and Ce^{4+} is small ($k_H/k_D = 1.1$ and 1.2 respectively), which indicates a one-electron decarboxylation mechanism. The considerable isotope effect on treatment with chromic acid (Cr^{6+}) ($k_H/k_D = 8.6$) and the high activation energy for the decarboxylation of α-hydroxybutyric acid suggest, according to the authors[130], a two-electron reaction mechanism. In terms of their influence on the rate of decarboxylation of the acids RCH(OH).COOH and $R_2C(OH)COOH$ under the influence of one-electron oxidants, the substituents fall within the sequence $C_6H_5 \gg CH_3 > H$. The kinetics of the oxidation of nine substituted mandelic acids with potassium permanganate in acid media have been investigated[131].

Kinetic studies on the decarboxylation of a series of α-hydroxyacids by lead tetra-acetate in glacial acetic acid have shown[132] that the reaction obeys a second-order kinetic equation and leads to the formation of aldehydes and ketones. The influence of substituents in the aromatic ring on the rate of decarboxylation is small. A considerable difference between the rates (by a factor of 240) has been observed only for lactic and benzilic acids. Strong acids have an insignificant influence on the oxidation of mandelic acid by lead tetra-acetate in glacial acetic acid, while basic compounds such as water, methanol, DMF, triethylamine, 2,4-lutidine, and acetate salts catalyse this reaction[133].

Three mechanisms have been proposed for the oxidative decarboxylation of α-hydroxyacids: radical, ionic, and synchronous[132,133]. The isotope effects obtained earlier[130] in the oxidation of mandelic acid by Mn^{3+} and Ce^{4+} indicate a radical mechanism, but experiments with radical-trapping agents—benzoquinone and mercury(II) chloride—in the oxidation of mandelic acid by lead tetra-acetate[132] indicate an ionic reaction pathway. An ionic mechanism was also proposed for the oxidative decarboxylation of 2-hydroxy-1,2,2,-triphenylpropionic acid[54]. The authors believe[54] that the formation of a ketone and an acetate supports the involvement of carbonium ions in the reaction. However, the synchronous mechanism appears to be the most acceptable[132]:



The isotope effect of the solvent in the reaction in deuterated acetic acid ($k_H/k_D = 0.63$) as well as the weak influence of the solvent polarity on the rate of decarboxylation of mandelic acid support the view that the decomposition of a cyclic complex takes place in the rate-limiting stage of the reaction. The values of $\Delta S^{\neq}$ obtained in the oxidation of α-hydroxyisobutyric, mandelic, and benzilic acids, which are respectively +9, +1.7, and +12 e.u., are believed by the authors to correspond to a mechanism postulating that several new species are formed in the rate-limiting stage from a cyclic intermediate.

The oxidative decarboxylation of mandelic acid by periodate[134] and of malic acid by cerium sulphate[135] was also believed by the authors of the investigations to include the reversible formation of a cyclic complex.

III. PHOTOCHEMICAL DECARBOXYLATION

The photolysis of cerium(IV), lead(IV)[57] and thallium(III)[25] carboxylates has been carried out by irradiating with light at wavelengths of 3500 and 2537 Å in the absence of oxygen in non-aqueous solvents. The photochemical homolysis of metal carboxylates leads to the formation of acyloxy-radicals, which are known[136] to decompose readily into the radical R· and CO_2:

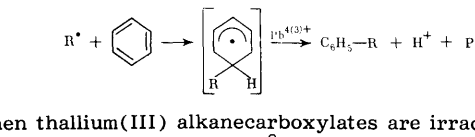
$$M^n(OCOR)_n \rightarrow M^{n-1}(OCOR)_{n-1} + RCOO\cdot \quad ;$$
$$RCOO\cdot \rightarrow R\cdot + CO_2 \quad .$$

The rate constant for the decomposition of $C_6H_5COO\cdot$ has been found by NMR (from CINP data) and proved to be $1 \times 10^8\ s^{-1}$.[137]

The intermediate reduced forms of thallium carboxylates $Tl^{II}(OCOR)_2$ [138] and lead carboxylates $Pb^{III}(OCOR)_3$ [32] are unstable and rapidly decompose further into the radical R· and stable reduced forms of the metal carboxylates:

$$M^{n-1}(OCOR)_{n-1} \rightarrow M^{n-2}(OCOR)_{n-2} + R\cdot + CO_2 \quad .$$

The interaction of radicals with the solvent and their dimerisation lead to the formation of alkanes, arylalkanes, and recombination products. When the radicals formed interact with hydrogen donors (chloroform, cumene, and isobutyric acid), the yield of alkanes increases. It has been suggested[15] that arylalkanes are obtained by the oxidation of an intermediate complex of the radical with the solvent—benzene:



When thallium(III) alkanecarboxylates are irradiated with light at a wavelength of 2537 Å, a higher yield of radical dimerisation products is observed than at 3500 Å. The authors explain this by the higher local concentration of free radicals under the conditions of the higher irradiation energy.

In the photodecarboxylation of thallium(III) carboxylates the yield of alkenes depends on the group R in the carboxylic acid and decreases in the sequence tertiary > secondary > primary[25]. The acids in which the COOH group is linked to a tertiary alkyl substituent are decarboxylated by lead tetra-acetate in benzene on irradiation at 3500 Å and room temperature much faster and with a higher yield than in the thermal oxidative decarboxylation (81 °C).[57] The compositions of the products do not differ greatly under these conditions and only some increase of the yield of alkanes is observed. The photochemical decarboxylation of cyclobutanecarboxylic acid also leads to a somewhat higher yield of cyclobutane than the thermal oxidative decarboxylation[93].

When thallium salts of carboxylic acid are irradiated at 2537 Å, a greater amount of alkenes is always obtained than at 3500 Å. This, as well as the fairly high yield of alkenes

(up to 10%) in the photodecarboxylation of $Tl(OCOR)_n$, where R is a primary group, indicates, according to the authors[25], that alkenes are formed as a result of the disproportionation of alkyl radicals:

$$2R^{\cdot} \rightarrow R(-H) + RH \quad .$$

The decrease of the yield of alkenes and esters obtained from the acids in the series based on R (tertiary > secondary > primary) shows that the reaction proceeds via the mechanism

$$Tl^{3+} + R^{\cdot} \rightarrow Tl^{2+} + [R^{+}] \text{ etc.}$$

In the presence of Cu^{2+} the mechanism changes:

$$R^{\cdot} + Cu^{2+} \rightarrow R(-H) + Cu^{+} + H^{+} ;$$
$$Cu^{+} + Tl^{3+} \rightarrow Cu^{2+} + Tl^{2+} \quad .$$

The rates of photochemical decarboxylation of the acids RCOOH with primary, secondary, and tertiary groups R on treatment with Ce^{4+} differ little[29]. On treatment with Pb^{4+}, [15,57] a significant difference is observed between the rates of decarboxylation in accordance with the sequence pivalic acid > isobutyric acid > butyric acid, which is probably associated with the increase of the activation energy for the homolysis of the bond in the lead carboxylates in this sequence.

In addition to pyridine and lithium acetate and trifluoroacetate in the photochemical oxidative decarboxylation of butyric acid by Ce^{4+} does not have an appreciable influence on the rate of reaction[29], while the addition of strong acids ($HClO_4$, BF_3, CF_3COOH) increases the rate appreciably. In the latter case the yield of alkenes and esters increases and the amount of alkanes falls. Oxygen decreases significantly the rate of reaction and lowers the yield of alkanes in photodecarboxylation by lead tetra-acetate[57]. Under these conditions, products of the oxidation of the radical by oxygen appear:

$$(CH_3)_3C^{\cdot} + O_2 \rightarrow (CH_3)_3COO^{\cdot} ;$$
$$2(CH_3)_3COO^{\cdot} \rightarrow O_2 + 2(CH_3)_3CO^{\cdot} \begin{cases} \rightarrow (CH_3)_3COOC(CH_3)_3 \\ \xrightarrow{SH} (CH_3)_3COH + S^{\cdot} \\ \rightarrow (CH_3)_2CO + CH_3^{\cdot} \end{cases} .$$

When pivalic acid interacts with lead tetra-acetate in the presence of oxygen, the formation of di-t-butyl peroxide (3%), acetone (9%), and t-butyl alcohol (78%) is observed.

The formation of free radicals in the photochemical decarboxylation of carboxylic acids by lead tetra-acetate has also been demonstrated by EPR.[57] Irradiation in the cell of the spectrometer of solutions of lead carboxylates in acids, benzene, or pyridine, from which oxygen had not been removed, led to the detection of alkylperoxy-radicals derived from pivalic, 2,2-dimethylbutyric, 2,2-dimethylvaleric, and 2,2-dimethyloctanoic acids (singlet, $g = 2.0152$).

The chain mechanism of the photochemical decarboxylation of carboxylic acids has been demonstrated in the determination of the quantum yield. In the oxidation of pivalic and dimethylbutyric acid by lead tetra-acetate the exact quantum yield could not be measured, but, according to a preliminary estimate, the chain length is approximately 200.[57] The quantum yield in the photochemical decarboxylation of acids by Ce^{4+} depends on the concentration of the latter and on the type of acid. At a 0.1M concentration of cerium acetate and 3500 Å a quantum yield is 1.11 ± 0.07 for pivalic acid, 0.81 ± 0.05 for isobutyric acid, and 0.52 ± 0.05 for butyric acid.

The photochemical decarboxylation of dibasic acids (succinic, glutaric, and adipic) on treatment with a 0.02M $FeCl_3$ solution (3500 Å, 38 °C) proceeds

$$HOOC(CH_2)_nCOOH \xrightarrow[2\text{-}6\ \text{days}]{FeCl_3, h\nu} \begin{cases} \rightarrow Cl(CH_2)_2COOH\ (78\%),\ n=2 \\ \rightarrow \text{(cyclic ketone)} + \text{(cyclic alcohol)}COOH\ (80\%),\ n=3 \\ \rightarrow Cl(CH_2)_4COOH\ (70\%),\ n=4 \end{cases} .$$

As a result of the reaction, chloro-substituted monobasic acids are formed from succinic and adipic acids, while glutaric acid leads mainly to γ-butyrolactone and a certain amount of a hydroxyacid. In the absence of $FeCl_3$ and in the dark the reaction does not take place. Special experiments have shown that neither β-hydroxypropionic nor γ-chlorobutyric acid are intermediates.

The decarboxylation of metal acetates, mainly mercury acetates, which proceeds with formation of organometallic compounds, has been considered in detail in a monograph[19]. The most probable mechanism of the photodecarboxylation of mercury salts of carboxylic acids (in benzene and acetic acid as solvents) is described by the following equations.

$$(RCOO)_2Hg \rightarrow RCOO^{\cdot} + {}^{\cdot}HgOCOR ;$$
$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 ;$$
$$R^{\cdot} + {}^{\cdot}HgOCOR \rightarrow RHgOCOR ;$$
$$R^{\cdot} + (RCOO)_2Hg \rightarrow RHgOCOR + RCOO^{\cdot} ;$$
$$2\,HgOCOR \rightarrow Hg_2(OCOR)_2 ;$$
$$Hg_2(OCOR)_2 \rightarrow Hg + (RCOO)_2Hg .$$

In this mechanism the $R^{\cdot} + (RCOO)_2Hg + RHgOCOR + RCOO^{\cdot}$ state, which presupposes a chain reaction mechanism, has not been supported by direct evidence. The photochemical reaction leads to the formation of a considerable amount of mercury(I) salts and organomercury compounds. In addition, similar reactions of free radicals result in the formation of saturated and unsaturated hydrocarbons [Eqn.(2)] as well as metallic mercury. The reaction is of preparative interest for the synthesis of alkylmercury salts. Mercury salts of aromatic acids are decarboxylated with much greater difficulty than the salts of aliphatic acids.

The decomposition of lead tetracarboxylates $(RCOO)_4Pb$ ($R = C_6H_5$, $o\text{-}CH_3C_6H_4$, $p\text{-}CH_3C_6H_4$, $o\text{-}O_2NC_6H_4$, $p\text{-}O_2NC_6H_4$, C_6H_{11}, or C_5H_9) in benzene by ultraviolet light or peroxides[140] is hindered when a substituent is present in the benzene ring of the arenecarboxylic acid. The radicals $RCOO^{\cdot}$, generated in the reaction, react with one another: $2RCOO^{\cdot} \rightarrow RCOOR + CO_2$, or decompose into CO_2 and radicals $R^{\cdot}$, which interact with benzene, leading to the formation of biaryls and disproportionation products.

IV. INITIATED DECARBOXYLATION

The initiated decarboxylation of aromatic acids (benzoic and toluic) in aprotic solvents (*o*-dichlorobenzene, nitrobenzene) takes place in the presence of oxygen and t-butyl peroxide or t-butyl hydroperoxide at temperatures sufficiently high to cause the homolysis of the peroxide (125 to 200 °C).[141,142] It has been suggested that the reaction mechanism involves the formation of aroyloxy-radicals when the acid interacts with a radical:

$$ArCOOH + X^{\cdot} \rightarrow ArCOO^{\cdot} + HX \quad .$$

Since the reaction does not take place in the absence of oxygen, it has been postulated that the radicals obtained from the initiator (methyl and t-butoxy-radicals, etc.) do not abstract hydrogen from the carboxy-group. Peroxy- and hydroxy-radicals (X = RCOO· or HO·) are apparently reactive. The aroyloxy-radicals are readily decomposed into CO_2 and an aryl radical, which interacts with the molecules of the aromatic solvent to form biphenyls. The initiated decarboxylation is catalysed by cobalt(III) naphthenates probably as a result of the direct oxidation of the acid by metal ions. The yield of biphenyl reaches 50% in this case.

Mercury salts of carboxylic acids are decarboxylated by acetyl, di-t-butyl, benzoyl, etc. peroxides or ultraviolet light with formation of organomercury compounds[19,143]. The reaction is carried out in acetic acid, benzene, and their mixtures at 80–98 °C:

$$RCOOHgOOCR + R'^{\cdot} \rightarrow R'HgOCOR + RCOO^{\cdot} \quad ;$$
$$RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2 \quad .$$

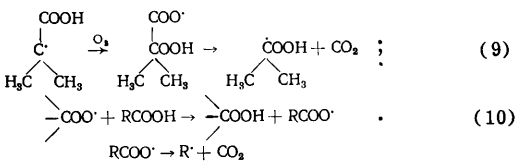
It has a radical chain mechanism, as shown by the virtually quantitative conversion of the mercury salts of carboxylic acids for comparatively small amounts of peroxy-compounds (molar ratio mercury carboxylate : peroxide ≅ 6 : 1) and also by the presence of small amounts of alkanes and alkenes in the reaction products. The mercury salts of lower representatives of homologous series of alkanecarboxylic acids react more readily than the salts of the higher and aromatic acids. The introduction of substituents into the aromatic ring prevents the decarboxylation of the mercury salts of aromatic carboxylic acids. The introduction of electronegative substituents into the molecule of an aliphatic mercury carboxylate also hinders the initiated decarboxylation reaction, the magnitude of the effect diminishing as the substituent becomes more remote from the carboxy-group[19].

Mercury(I) salts also react with diacyl peroxides, forming organomercury compounds:

$$RCOOHg-HgOOCR + (R'COO)_2 \rightarrow 2R'HgOCOR + 2CO_2 \quad .$$

A series of organomercury compounds have been obtained with the aid of these reactions: the salts of aryl-, methyl-, ethyl-, and propyl-mercury[143], cyclopropyl- and cycloheptyl-mercury[144], cyclohexyl- and cyclopentyl-mercury[145], n-butyl-, n-pentyl-, and n-nonyl-mercury[146], and α-naphthylmercury[147].

The decarboxylation of carboxylic acids is frequently accompanied by the liquid-phase oxidation of organic compounds. Data for this process, which is called "decarboxylation coupled with oxidation" or "oxidative decarboxylation", have already been surveyed[20,148] and will not be considered in this review. One should note that such reactions can also be classified as initiated decarboxylation, since the decarboxylation takes place under the influence of radicals obtained by the oxidation of organic admixtures or the carboxylic acids themselves. The mechanism of reactions of this kind can include intramolecular decarboxylation [reaction (9)], when the molecules being oxidised are also decarboxylated, and intermolecular decarboxylation [reaction (10)], when molecules of one type are oxidised and those of another are decarboxylated:



(9)

(10)

V. THE EFFECT OF LIGANDS IN THE OXIDATIVE DECARBOXYLATION OF CARBOXYLIC ACIDS

Strong acids accelerate the decarboxylation of carboxylic acids under the influence of Pb^4,[32,57] Mn^{3+},[28] Co^3,[27] and Tl^{3+}[25] ions. This effect is attributed to the formation of cationic complexes, which are stronger oxidants than their neutral analogues:

$$M(O_2CR)_n + H^+ \rightleftharpoons M(O_2CR)_{n-1}^+ + RCO_2H \quad .$$

The decarboxylation of alkanecarboxylic[15,31] and dicarboxylic[109] acids by lead tetra-acetate in benzene is appreciably accelerated in the presence of pyridine. The acceleration of the reaction in the presence of acetate and trifluoroacetate has been observed in the decarboxylation of acids by Co^{3+},[27] and Mn^{3+}[28] ions. The influence of acetate ions on the rate of reaction has been explained by the formation of labile complexes of the type $[Pb^{IV}(OAc)_6^{2-}$,[149] $[Co_2^{III}.(O_2CR)_7^-]$, and $[Co^{III}(O_2CR)_4^-]$.[27] Spectrophotometric measurements have shown that the addition of 3 M $LiOCOCH_3$ to lead tetra-acetate in acetic acid causes a hypsochromic shift in the ultraviolet spectrum (there is a shoulder at 280 nm), which increases after the addition of small amounts of triethylamine.

Certain complexes of lead carboxylates with pyridine have been isolated and investigated[149]:

$$Pb(OAc)_{4-n}(O_2CR)_n + m\,Py \rightleftharpoons Pb(OAc)_{4-n}(O_2CR)_n Py_m \quad .$$

There exists a view[15] that the accelerating influence of pyridine is associated with the fact that the formation of metal carboxylates is facilitated in the pre-equilibrium stages:

$$Pb(OAc)_4 + n\,RCO_2H \rightleftharpoons Pb(OAc)_4 HOCOR\ ;$$
$$Py + Pb(OAc)_4 HOCOR \rightleftharpoons PyH^+ + Pb(OAc)_4 OCOR^-\ ;$$
$$Pb(OAc)_4 OCOR^- \rightleftharpoons OAc^- + Pb(OAc)_3 OCOR\ .$$

The oxidative decarboxylation of mandelic acid by lead tetra-acetate in acetic acid is catalysed by different basic compounds such as water, methanol, DMF, 2,6-lutidine, 2,4-lutidine, triethylamine, and acetate salts[133]. The process consists of two fluxes, one of which constitutes the non-catalytic reaction and the other the base-catalysed reaction. In the range of concentrations up to 3M for methanol and up to 1M for water, the reaction is of first order with respect to methanol and water. At higher concentrations of the additives the reaction order increases to two. The concentrations of acetate salts and amines are included in the kinetic equation with an exponent close to unity. In terms of their catalytic effect, the additives can be arranged in the following sequence [the values of k_2 (litre mol^{-1} s^{-1}) are indicated in brackets]: H_2O (0.065) < CH_3OH (0.13) < LiOAc (73.5) < NaOAc (193) < KOAc (263). The catalytic action of bases is explained by the modification of the oxidant as a result of the change in the ligand environment of the lead ion. Apart from kinetic relations, this is indicated by a series of physicochemical measurements. When lead tetra-acetate is dissolved in methanol, the brown-red colour of the complex appears and then vanishes after the addition of 5% acetic acid without loss of the oxidising properties of the oxidant. Furthermore, the complex $Pb(OAc)_2(OCH_3)OH$ has been isolated from methanol and characterised. The relative catalytic activities of acetate salts decrease in the sequence KOAc > NaOAc > LiOAc, i.e. with decrease of the degree of dissociation of the ion pairs into ions[150,151]. However, it has been suggested that, apart from ions, ion pairs also exhibit a catalytic effect in the reaction. Since amines can participate in the formation of acetate ions (in accordance with the equation $Py + HOAc \rightleftharpoons PyH^+OAc^-$), which accelerate the reaction, their catalytic effect is difficult to isolate in a pure form. Acrylonitrile accelerates the reaction to a greater extent than acetonitrile, which indicates a specific effect of bidentate ligands.

The catalytic decarboxylation of dicarboxylic β-ketoacids has been reviewed[152-154]; in view of its specificity, this reaction will not be considered here. It is also characterised by catalytic effects of basic ligands (pyridine, quinoline, bipyridyl, phenanthroline, etc.). The explanation of the catalytic effects in these reactions given by Bonchev[155] can also be applied to the oxidative decarboxylation of carboxylic acids with the aid of transition metal ions. The accelerating effects of π-ligands have been explained[155] by the presence of a reverse π-dative bond between the metal and the ligand (M → L), which increases the positive charge of the metal ion and hence increases its catalytic activity. The interaction of the metal ion with the ligand has been confirmed experimentally by NMR and also by absorption spectroscopy and EPR.

The effect of ligands should be significant also in the second stage of the decarboxylation involving successive oxidation of the free radicals formed in the first stage of the reaction. This is indicated particularly by Kochi's study[156] of the oxidation of alkyl radicals by copper(II) salts. The replacement of the acetate ligand by the weakly coordinated perchlorate and triflate ligands in the oxidation of radicals in acetic acid results in a sharp decrease of the yield of alkenes. When the n-butyl radical is oxidised by $Cu(ClO_4)_2$ and $Cu(O_3SCF_3)_2$, the amount of alkenes falls to 34.1% (compared with the 94% yield of alkenes in the oxidation by copper acetate) with a simultaneous increase of the yield of alkyl acetates. Analysis of the composition of the products of the oxidation of radicals by various copper(II) salts led the authors[156] to the conclusion that the acetate ligand promotes oxidative elimination, which increases the yield of alkenes; on the other hand, the capacity for oxidative solvolysis increases with increase of the stability of the carbonium intermediate, which is also promoted by weakly coordinated ligands such as perchlorate and triflate.

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