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JAN 23 1967

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PHOTO-INDUCED REDOX REACTIONS

Biennial Report

Case Institute of Technology

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Contract Number: AF-AFOSR 226-63

Period covered: January 1, 1963 - December 1, 1966

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## PART I. PHOTOLYSIS OF METAL ION COMPLEXES OF OLEFINS

### 1. Introduction

The objective of this program has been to examine the photolysis of various metal ion complexes, and further to study the nature and scope of such reactions. Initially, olefin complexes of silver salts were studied. In these investigations, the photolyses were conducted near room temperature using unfiltered ultraviolet light from high pressure mercury lamps; no promoters were employed.

The work described in this report deals with the investigation of various solvents for the photolyses, the effect of the anion on the course of the photolysis of the silver ion complexes, and the nature of the reaction using various other metal salts and olefins. The photolyses were conducted in Vycor tubes sealed with rubber septum caps, using the unfiltered irradiation from an air-cooled, high-pressure mercury vapor lamp (General Electric H-100-A4).

### 2. Photolyses of Olefin Complexes of Silver Ion

Silver ion-olefin complexes were examined first because of the relative ease of photoreduction of silver salts and because of the previously accumulated knowledge of these complexes. (1-4)

#### 2.1 Silver Nitrate

Of the silver salts commonly employed in olefin complex formation, perhaps the nitrate has been most employed. 1,5-Cyclooctadiene (COD), a "chelating" diolefin, forms complexes with various metals and appeared quite amenable to photoreaction. Hence cyclooctadiene was employed most often in these studies.

The silver nitrate-1,5-cyclooctadiene complex was prepared according to a published procedure. (1) To a solution of 50 g. silver nitrate in 100 ml. distilled water prepared in a stoppered low-actinic § Erlenmeyer flask was added 10 ml. freshly distilled 1,5-cyclooctadiene. The two-phase mixture was vigorously shaken for ca. 10 minutes. A white solid formed. The flask was heated until all the solid had dissolved; the flask was then cooled in ice.

The mixture was filtered and the complex was recrystallized from 95% ethanol and was kept in a vacuum desiccator over shaved paraffin saturated with cyclooctadiene and protected from light.

a) 1,5-Cyclooctadiene. A saturated solution of the silver nitrate-1,5-cyclooctadiene complex in 1,5-cyclooctadiene was degassed, nitrogen was admitted to atmospheric pressure, and the solution irradiated 36 hrs. During this time, samples of the reaction mixture were periodically withdrawn with a microsyringe and analyzed by gas-liquid chromatography (GLC) on an Aerograph HyFi 600-A using a 12 ft. column of 15% diisodecyl phthalate, 5% Bentone 34 on Chromosorb W at 150°C and 10 psi N<sub>2</sub>. At no time during the photolysis nor at the end were any peaks other than the solvent peak observed.

b) Diethyl ether. A mixture of 1.00 g. of the AgNO<sub>3</sub>-COD complex in 9 ml. anhydrous diethyl ether was heated in warm water until the ether was boiling and was stoppered with a rubber septum cap; then 0.2 ml. 1,5-cyclooctadiene was added through the cap. The undissolved complex was protected from light by wrapping the bottom portion of the tube with aluminum foil. After 72 hours irradiation no detectable change in composition of the solution could be observed by GLC.

c) Ethanol. A saturated solution of the AgNO<sub>3</sub>-COD complex in ethanol containing added 1,5-cyclooctadiene was irradiated 116.5 hrs. Again no peaks other than those attributable to solvent and COD were detected by GLC.

d) Tetrahydrofuran. A saturated solution of the AgNO<sub>3</sub>-COD complex in tetrahydrofuran containing added 1,5-cyclooctadiene was irradiated 115.5 hrs. No peaks other than those attributable to solvent and COD were detected by GLC.

## 2.2. Silver Tetrafluoroborate

To avoid hydrolysis of the silver tetrafluoroborate by the moisture in the air, reaction solutions involving this salt were prepared in a dry nitrogen filled "dry box".

a) 1,5-Cyclooctadiene. To 1 g. silver tetrafluoroborate was added 6 ml. COD. Upon mixing the olefin and the silver salt, heat was generated and the white silver salt darkened slightly to yellow-brown. After thorough mixing, the undissolved silver salt and/or complex, which had settled at the bottom of the photolysis tube, appeared to be a hard mass. Photolysis of the mixture for 72 hours afforded no products detectable by GLC.

b) Diethyl ether. To 1.0 g. silver tetrafluoroborate in a stoppered Vycor tube was added 5 ml. anhydrous ether. Heat was evolved and the silver salt dissolved. Two layers were formed. As the first drops of COD were added, a voluminous, white precipitate was formed. In all 1 ml. of COD and 3 ml. more ether were added. The white material was protected from the irradiation by aluminum foil. After 20 hrs. irradiation, an additional 2 ml. COD was injected into the reaction mixture. After a total of 160 hours photolysis, no peaks other than those attributable to ether and COD were detectable by GLC.

c) Acetonitrile. Acetonitrile (5 ml.) was added to 1.0 g. silver tetrafluoroborate. The silver salt went into solution with great evolution of heat. 1,5-Cyclooctadiene (1.0 ml.) was added. The homogeneous solution was irradiated 208 hrs. After this time, only peaks attributable to solvent and COD were detectable by GLC.

### 2.3 Silver Perchlorate (s)

a) Diethyl ether. A saturated solution of silver perchlorate monohydrate in ether was prepared. COD was injected portionwise until no more white material formed. Irradiation of 10 ml. of the ethereal solution for 71 hrs. produced no new peaks on GLC analysis.

b) Acetonitrile. A saturated solution of the dried, ether-free, solid material formed in (a) above in acetonitrile was irradiated 69 hrs. Again, GLC analysis revealed no peaks other than those attributable to acetonitrile and COD.

c) Water. To a solution of silver perchlorate (0.451 g.) dissolved in 5 ml. distilled water was added 0.122 ml. COD. The mixture was thoroughly shaken and let stand overnight for the white solid to settle. More water (10 ml.) was added and the stoppered tube was irradiated 190 hrs. At this time there was a slight deposit of silver metal on the inside of the tube. The contents of the tube were poured into ether and the ether solution washed with water. Analysis of the ethereal solution by GC indicated no components other than ether and COD.

### 2.4 Silver Trifluoroacetate (6)

The silver trifluoroacetate complex of cyclooctadiene was prepared by dissolving 8.0 g. silver trifluoroacetate in 16 ml. water and adding 5.0 ml. cyclooctadiene. After vigorous shaking, the complex was filtered on a sintered glass funnel, washed with water and dried overnight in a vacuum desiccator.

a) Diethyl ether. A saturated solution of the above formed silver trifluoroacetate-cyclooctadiene complex was prepared. A 12 ml. portion of this solution and 0.12 ml. COD were mixed and the resulting solution was

irradiated 96 hrs. Again GC analysis showed no components of the solution except ether and COD.

To a solution of 0.3 g. silver trifluoroacetate in 3.0 ml. ether was added 1.0 ml. COD. A gelatinous looking material formed and the mixture was thoroughly shaken. After irradiation for 120 hrs. a coat of metallic silver had formed on the inner surface of the tube. The solution was poured into water, the layers were separated, and the ether solution was washed three times with 20 ml. water and dried over sodium sulfate. The ether solution was brownish-yellow; however, GC analysis showed no detectable change in the composition of the organic materials.

b) Acetonitrile-diethyl ether. To 2 ml. of a saturated solution of the silver trifluoroacetate-COD complex dissolved in acetonitrile was added 0.01 ml. COD and 2 ml. ether. After 90 hrs. irradiation, no reaction products were detectable by GC analysis.

c) Tetrahydrofuran. To 0.5 g. silver trifluoroacetate in a photolysis tube, COD was added 1.0 ml. at a time until 5.0 ml. had been added. After the first ml. COD was added and the mixture stirred, a thick white mass formed. Each successive addition of COD thinned the mass, but not all dissolved. After 2.0 ml. tetrahydrofuran was added, the solution was homogeneous. After irradiation of this solution for 68 hrs., GC analysis showed only a very minor new component in addition to tetrahydrofuran and COD.

## 2.5 Other Silver Salts

The silver salts used in photolyses described in this section were investigated only in diethyl ether as solvent.

a) Silver p-Toluenesulfonate. The silver salt (0.20 g.) was shaken with 3 ml. diethyl ether. A small amount of the salt appeared to

dissolve. Upon addition of 1.0 ml. 1,5-cyclooctadiene and additional agitation, more of the tosylate appeared to dissolve. After 114 hrs. of irradiation, no new components could be detected by GC analysis of the solution although a slight deposit of silver metal was present on the inner surface of the photolysis tube.

b) Silver Acetate. This silver salt (0.30 g.) was shaken with 3.0 ml. ether. Some of the salt dissolved. After addition of 1.0 ml. COD, the complex precipitated and after additional shaking the mixture was irradiated. After 120 hrs. an additional 4.0 ml. ether was added. After irradiating for 144 hrs., analysis by GC showed no reaction products.

c) Silver Benzoate. Silver benzoate was added to 10 ml. ether and 2 ml. COD added. No precipitate indicative of the silver-olefin complex appeared. After photolysis for 54 hrs., no reaction products were detectable by GC analysis. The silver benzoate was apparently insoluble in ether so that a complex with the cyclooctadiene was not formed.

### 3. Photolyses of 1,5-Cyclooctadiene in the Presence of Other Metal Ions

#### 3.1 Mercury(II) acetate (7,8)

a) To 3.19 g. mercuric acetate in 5 ml. ether was added 0.614 ml. cyclooctadiene. This mixture was allowed to stand at room temperature 43 hrs. Then 5 ml. of a saturated solution of mercuric acetate in COD was added. This solution was photolyzed 93 hrs.; no reaction product was detectable by GC analysis

b) Ten ml. of an ether solution saturated with mercuric acetate and 2.0 ml. of COD were mixed and photolyzed 93 hrs. No reaction products were detectable by GC analysis.

c) A saturated solution of mercuric acetate in 1,5-cyclooctadiene was irradiated 93 hrs. Peaks attributable only to the COD were observed on GC analysis.

d) Mercuric acetate (6.37 g.) was dissolved in 75 ml. methanol. To this solution was added 2.5 ml. COD and this mixture was protected from light and was allowed to stand at room temperature 46 hrs. The solution was filtered and the methanol was removed by gentle warming and reduced pressure (rotary evaporator). The resulting thick, clear gum was dissolved in chloroform, washed 4 times with 5% sodium carbonate, three times with water and was dried over sodium sulfate. Removal of the chloroform left 3.33 g. of a very viscous, orange gum. This gum was dissolved in ether and was irradiated 181 hrs. During this time, a gray solid formed along the sides of the tube. The solid finally formed small droplets of metallic mercury. However, no organic reaction product could be found by GC analysis .

e) A solution of 25.48 g. mercuric acetate in 75 ml. methanol was heated gently and stirred magnetically. After dissolution of the mercuric acetate, 4.41 g. 1,5-cyclooctadiene was added and stirring was continued 89 hrs. Ether was added to the solution and the solution was washed with water. The ether solution was dried and the ether removed, leaving 22.64 g. of a thick gum.

(1) 5.0 g. of the above prepared methoxymercuriacetate was dissolved in 11 ml. of glacial acetic acid and the solution was irradiated. A white, micaceous precipitate (apparently mercury(I) acetate) slowly formed during one week. Further irradiation caused the slow appearance of a gray precipitate, apparently metallic mercury. Total time of irradiation was 554 hrs. Despite the deposition of the inorganic solids, no organic reaction products could be detected by GC analysis. Although the molar ratio of mercury

acetate to cyclooctadiene was 2:1, complete methoxymercuration of the olefin cannot be assumed.

(2) A 5.0 g. sample of the methoxymercuriacetate compound was dissolved in 12 ml. acetone. Irradiation of the solution caused metallic mercury to be deposited with no intermediate formation of mercury(I) acetate. After a total irradiation time of 553 hrs., no organic reaction products could be detected by GC analysis.

### 3.2 Iron(III) Chloride

a) A saturated solution (10 ml.) of anhydrous iron(III) chloride in anhydrous ether and 2 ml. of cyclooctadiene were irradiated 51 hrs. Analysis by GC showed at least five components in the photolysate in addition to ether and cyclooctadiene. A black material formed on the inside of the photolysis tube on repetition of this photolysis.

b) Two hundred ml. of ether was saturated with iron(III) chloride and 40 ml. of COD was added. This solution was irradiated in a Pyrex vessel with the lamp (a General Electric H100-A4) suspended in a Vycor well immersed in the center of the photolysate. The lamp and the solution were cooled by passing water through a jacket between the lamp well and the solution being irradiated. During the irradiation a black solid deposited on the surface of the water-cooled chamber. After 42 hrs., this material was scraped off the sides of the water chamber and photolysis was continued for a total of 68 hours. More black material had formed; this was scraped off and added to the first solid obtained.

The ethereal solution was poured into water. The combined black solids were slurried three times with ether and these ether washings added to the main ethereal solution. This ether solution was washed six times with deionized water and dried over sodium sulfate. The ether was removed. The residual

liquid showed the presence of chloride by sodium fusion test. A portion of this liquid was hydrogenated in ethyl acetate using 10% palladium on charcoal catalyst. Withdrawal of samples at intervals during the hydrogenation showed all reaction products disappeared with the simultaneous appearance of cyclooctane and cyclooctene. After absorption of hydrogen stopped, cyclooctane was the only component. This reaction apparently produced variously chlorinated cyclooctane and/or cyclooctene derivatives.

### 3.3 Iron Pentacarbonyl<sup>(9)</sup>

A solution of 1.0 ml. freshly distilled iron pentacarbonyl, 10 ml. ether and 1.0 ml. cyclooctadiene was irradiated 98 hrs. Originally, the solution was orange-brown in color; after 1 day of photolysis, the solution was green. Analysis of the orangish solution by GC showed no new peaks attributable to reaction products. The cyclooctadiene used had two very minor impurities in it (< 0.5%) which could not be removed by distillation. One of the impurities in the cyclooctadiene appeared to increase in quantity during this photolysis.

### 3.4 Cobalt(II) Bromide

Anhydrous cobalt(II) bromide was dissolved in anhydrous ether to give a saturated solution. A mixture of 10 ml. of the blue ethereal solution and 2 ml. of COD was photolyzed 98 hrs. A green-gray precipitate slowly formed. Analysis of the solution indicated no new components present.

### 3.5 Cobalt(II) Acetylacetonate

Cobalt acetylacetonate was dissolved in anhydrous ether to give a saturated solution. A mixture of 10 ml. of this solution and 2 ml. COD was irradiated 122 hrs. After this time no photoproducts were detectable by GC analysis.

### 3.6 Molybdenum Carbonyl

A saturated solution of molybdenum carbonyl in ether was prepared. A mixture of 10 ml. of the ethereal solution and 2 ml. COD was photolyzed 98 hours. A small brown precipitate had formed in the tube during this time. Analysis of the photolysate by GC indicated no photoproducts.

### 4. Summary and Conclusions

Despite the ease of formation of silver ion complexes of olefins, photolysis of a variety of these complexes in several solvents afforded no apparent photoreaction. The cuprous chloride-1,5-cyclooctadiene complex, the structure of which has been determined,<sup>(10)</sup> has been shown<sup>(11)</sup> to undergo photoreaction in ether solution at 2537Å to produce tricyclo[3.3.0.0<sup>2,6</sup>]octane. The apparent lack of reactivity of the silver complexes could possibly be attributed to 1) the increased stability of the silver complexes (compared to copper(I) complexes, the ones of silver are generally considered to be more stable)<sup>(2)</sup> and 2) the polychromatic light contained insufficient high energy light.

That the metal compounds other than mercury(II) acetate actually form complexes with the olefin was not ascertained. The methoxymercurial adduct described could be the diadduct, but a mixture of the mono- and di-adducts cannot be ruled out.

The apparent chlorination observed with anhydrous iron(III) chloride is similar to that observed with copper(II) chloride.<sup>(12)</sup>

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PART II. THE PHOTOREACTION OF HEAVY METAL ACETATES AND CARBOXYLIC ACIDS

1. Introduction

The thermal reaction of lead tetraacetate and carboxylic acids, commonly called "oxidative decarboxylation", has received extensive attention. Various workers have accounted for the observed products of the reaction by postulating ionic<sup>(1,2)</sup> and radical<sup>(3,4,5)</sup> intermediates. For others<sup>(6,7)</sup> a clear-cut distinction could not be made. A mechanism which incorporates both of these entities, a radical chain mechanism, was suggested by Kochi<sup>(8,9)</sup> to account for all of the products formed as well as for the effect of oxygen, copper(II) salts, and butadiene on the reactions with primary and secondary acids, e.g. valeric and 2-methylbutyric acids, respectively. Postulated<sup>(8,9)</sup> in this mechanism was an important lead(III) species. No direct evidence had been presented confirming such an intermediate and to obtain such evidence not only would provide substantial strength to the proposed mechanism but also would be of significant importance to the chemistry of lead.

The most obvious method of detecting a lead(III) species would be by electron spin resonance since lead(III) would be paramagnetic. Photolytic initiation appeared most attractive; therefore the similarity of the thermal reaction and the photolytic one had to be established.

Thallium is adjacent to lead in the periodic table and in its highest oxidation state, Tl(III), it is a 2-electron oxidant similar to, but not as strong as, lead(IV) in oxidative properties. This difference in the two metals indicated that the "oxidative decarboxylation" with thallium(III) may proceed by a mechanism analogous to the reaction with lead(IV), but may possess striking differences.

2. Comparison of the Thermal and Photolytic Oxidative Decarboxylation with Lead(V) Acetate

Since it was planned to use ultraviolet irradiation to induce decomposition of the lead(IV) carboxylates during the electron spin resonance studies, a comparison of the reaction products, both quantitatively and qualitatively, was necessary in order to determine the differences and similarities of the reactions.

2.1 Cyclohexanecarboxylic acid

Cyclohexanecarboxylic acid, a secondary acid, was the acid chosen to demonstrate the similarities of the two methods of conducting the oxidative decarboxylation because all of the products expected from its reaction would be liquids, except carbon dioxide, thus eliminating large volumes of gases.

2.1.1 Thermal Reaction

These reactions were run in duplicate. As an example of a typical run, 2.293 g. lead(IV) acetate (5.17 mmoles) and 2.924 g. cyclohexanecarboxylic acid (22.8 mmoles) were weighed into a 50 ml., 1-neck, round-bottomed flask equipped with a short side arm sealed with a rubber serum stopper. Benzene (20 ml.) was added and the mixture was stirred magnetically. While the solution was stirring, a water-cooled condenser, connected to mercury-filled gas-collecting tubes, was attached to the round-bottomed flask. After the golden-colored solution became homogeneous, nitrogen (introduced by a hypodermic needle through the septum in the side arm) was bubbled through the stirred solution for 10-15 minutes to purge both the solution and the system of oxygen. The needle was withdrawn and the flask was placed in a preheated heating mantle, controlled so that the temperature of the liquid in the flask would attain a temperature just above the boiling point of benzene (ca. 85°). The pressure in the closed system was maintained at atmospheric pressure by adjusting the level of the mercury in the collecting tubes to the level in the mercury reservoir. After the solution attained reflux, the progress of the reaction was followed by measuring the gas evolution. The volume increase due to expansion was taken into consideration. When gas evolution ceased (123 ml. collected) and the solution was colorless, the reaction was considered complete. The system was allowed to cool to room temperature and the gases above the solution were analyzed qualitatively by GC on a 12 ft. silica gel column at 0° for carbon dioxide. Methane was not detected. The solution was diluted to 30 ml. with glacial acetic acid.

Products were analyzed by gas-liquid chromatography using the internal marker system. It was found that n-hexane was a suitable marker for cyclohexane and cyclohexene when employing 12-ft. column of 15% didecylphthalate, 5% Bentone 34, on Chromosorb W at 75°C. Similarly, ethyl hexanoate was used as a marker for cyclohexyl acetate on a 9-ft. column of 20% diethyleneglycol succinate (DEGS) at 150°C. n-Butylcyclohexylcarboxylate was employed in determining the yields of phenylcyclohexane and cyclohexylcyclohexylcarboxylate on a 9-ft. diethyleneglycol succinate (DEGS) at 180°C. Appropriate volumes of benzene solutions of the respective markers of known concentration were added to aliquots of the diluted reaction mixture. This mixture was worked up by washing the solution four times with water, three times with 10% hydrochloric acid, five times with a saturated sodium bicarbonate solution, and three times with water; the solution was dried over anhydrous magnesium sulfate and was then analyzed by GC. The product spectrum is shown in Table I.

TABLE I. Yields of Products from the Thermal and Photolytic Decarboxylations of Cyclohexanecarboxylic Acid with Lead(IV) Acetate<sup>a</sup>

Method of Decarboxylation	% Cyclohexane	% Cyclohexene	% Cyclohexyl Acetate	% Cyclohexyl cyclohexanecarboxylate	% Phenyl Cyclohexane
Thermal (Sec.2.1.1)	14	38	20	13	10
Photolytic (Sec.2.1.2a)	21	27	8	3	2
Section 2.1.2b	23	29	10	5	?
Section 2.1.2c	24	32	13	4	2

a) All yields presented as moles of compound per mole of lead(IV) decomposed.

### 2.1.2 Photolytic Reactions

A stock solution was prepared in a 250 ml. volumetric flask from 28.82 g. lead(IV) acetate (65.0 mmoles), 38.44 g. (300 mmoles) cyclohexanecarboxylic acid, and benzene. After dissolution, the volume was adjusted to 250 ml. with benzene. Aliquots of this golden-colored solution were taken for photolysis by three different procedures.

a) A 155 ml. aliquot was placed in the photolysis apparatus described above in Part I, 3.2b. With cold water flowing through the jacket, nitrogen was bubbled through the solution 30 min. The solution was photolyzed 6 hrs. with the unfiltered light from a GE H100-A4 high-pressure mercury vapor lamp with the Pyrex sheath removed. The colorless solution was then diluted to 190 ml., marker solutions added to aliquots, and the whole worked up as previously described. The analyses were performed as previously described. The product spectrum is shown in Table I.

b) A 10 ml. aliquot was placed in a Vycor tube; nitrogen was bubbled through the solution 10 min. using a glass capillary and the tube was capped with a rubber serum stopper. This solution was photolyzed 7 hrs. with an air-cooled GE H100-A4 lamp with the Pyrex sheath removed. Marker solutions were added to the colored solution. The whole was worked up and the analyses were performed as before. The product spectrum is shown in Table I.

c) These photolyses were performed as described in (b) except that a Rayonet photochemical reactor was used. The wavelength of the light was  $2537\text{\AA}$ . The photolysis was carried out for 45 min. The product spectrum is shown in Table I. One tube left in the photochamber 24 hours had a rather large gray deposit on the inside of the photolysis tube. Apparently

during the longer exposure to this light lead(IV) is reduced completely to lead metal.

## 2.2 2,2-Dimethylbutyric Acid

A stock solution was prepared in a 50 ml. volumetric flask from 4.424 g. (9.98 mmoles) lead(IV) acetate and 10 ml. (80 mmoles) 2,2-dimethylbutyric acid and benzene. After dissolution the volume was adjusted to 50 ml. with benzene. Aliquots of this solution were treated in manners analogous to those described in 2.1 above.

a) A 10 ml. aliquot was placed in a Vycor tube. The stoppered tube was kept in an oil bath thermostatted at 80° until the solution was colorless (12.5 hrs.). After the reaction was complete, the solution was cooled and the appropriate volume of a solution of a known concentration of n-pentane in benzene was injected into the reaction solution through the septum with a hypodermic syringe, and the solution analyzed directly. n-Pentane had been previously established as an appropriate marker for the hydrocarbons produced in the reaction. During the analysis of the hydrocarbons on a 10-ft. 30% Dowtherm on firebrick column at 42°C, the sample tubes were kept in an ice bath to minimize the amount of hydrocarbons in the vapor phase. The solutions did not freeze. Only the hydrocarbons were determined. The yields are given in Table II.

b) A 10 ml. aliquot in a stoppered Vycor tube was placed in the Rayonet photoreactor and irradiated for 35 min. with 2537Å light. A slight gray deposit was noticed in the colorless solution. An appropriate volume of the marker solution (n-pentane in benzene) was injected into the reaction solution through the rubber septum with a hypodermic syringe and the solution analyzed as above. The yields of hydrocarbon products are given in Table II.

c) A 10 ml. aliquot in a Vycor tube was treated as described in (b) above, except that an air-cooled General Electric H100-A4 mercury vapor lamp was employed as the source of irradiation. The sample was irradiated 2.5 hrs. The yield of hydrocarbons are shown in Table II.

TABLE II. Yields of Hydrocarbons from the Thermal and Photolytic Decarboxylations of 2,2-Dimethylbutyric Acid<sup>a</sup>

Method of Decarboxylation	% 2-methylbutane	% 2-methyl-1-butene	% 2-methyl 2-butene
Thermal (Sec. 2.2a)	0	31	29
Photolytic (Section 2.2b)	9	55	37
(Section 2.2c)	trace	46	39

### 2.3 Observations and Conclusions

a) In the decarboxylation of cyclohexane carboxylic acid, the same products were obtained in the thermal reaction and in all of the photolytic ones. The esters and alkylbenzenes show the most pronounced differences in the two methods of decarboxylation; the combined yields of these components in the thermal reaction are over twice those obtained by any photolytic method. The hydrocarbons, i.e. alkane and alkene, do differ in amount, but the difference is not great. In all instances, the cyclohexene is more abundant than the cyclohexane and the combined yields of these components is fairly constant in all cases. Qualitatively, the thermal reaction and the photolytic ones appear to be the same; quantitatively, they appear similar.

b) The decarboxylation of 2,2-dimethylbutyric acid, a tertiary acid, showed a more obvious difference. In the thermal reaction no 2-methylbutane was produced; in the photolytic reactions, however, this product was found. Trace quantities were observed utilizing the high pressure

mercury lamp, whereas a substantial quantity, 9%, of the 2-methylbutane was found using 2537Å irradiation. It was shown that extended irradiation of the solution at this wavelength (see 2.2.b above) produced a sizeable quantity of 2-methylbutane, 75%, along with greatly enhanced amounts of the two olefins, 2-methyl-1-butene, 115%, and 2-methyl-2-butene, 60%. In these extended photolytic reactions, the lead(IV) appeared to be reduced to the metal. Because of this added complication, 2537Å light was not further used in decarboxylations with lead(IV) acetate.

The two olefins formed in these reactions differed somewhat in relative amounts and in total amount. The thermal and the photolytic reaction using the high pressure mercury lamp (General Electric H100-A4) appear to be the more similar when comparing only the alkanes and alkenes formed.

c) Further studies<sup>(10)</sup> directed toward establishing similarities between thermal and photolytic decarboxylations with lead(IV) acetate and acids were carried out in these laboratories in connection with oxygen inhibition studies with tertiary acids. The thermal reactions were performed in a manner analogous to that described in Section 2.1.1. The photolytic reactions were carried out in quartz tubes in the Rayonet photochemical reactor using the 3500Å region lamps for irradiation. More complete product analyses were performed with the two tertiary acids used. The results are shown in Table III.

These results<sup>(10)</sup> further indicate the similarity of the photolytic and thermal reactions. No substituted benzenes could be found in the photolytic reactions, but only very small amounts were present in the thermal runs.

d) From analysis of the product spectra, it was concluded that the thermal and photolytic decarboxylations of acids with lead(IV) acetate were sufficiently similar to warrant the use of light as the initiator of the decarboxylation reaction for the electron spin resonance studies.

TABLE III. Product Distribution of Thermal and Photolytic Decompositions of Tertiary Acids with Lead(IV) Acetate<sup>10</sup>

Product	Thermal (80°)	Photolytic (3500Å)
<u>Pivalic Acid</u>		
isobutene	48.0	73.6
t-butylacetate	9.2	15.1
t-butylpivalate	8.1	8.1
t-butylbenzene	0.4	0
<u>2,2-Dimethylbutyric Acid</u>		
2-methyl-1-butene	24.3	44.0
2-methyl-2-butene	25.0	36.1
t-amyl acetate	5.9	8.0
t-amyl-2,2-dimethylbutyrate	8.1	4.0
t-amylbenzene	0.3	0

### 3. Electron Spin Resonance Studies

Important steps in the mechanism proposed by Kochi<sup>(8,9)</sup> for the thermal decarboxylation of acids with lead(IV) acetate involved a lead(III) species. Since the lead(IV) is reduced to lead(II) during the reaction, this necessitates two one-electron changes in the lead. Lead(III) would have the electronic configuration  $X_e \text{ core: } 6s^1 4f^{14} 5d^{10}$ ; having one unpaired electron, lead(III) would be paramagnetic and should be observable by electron spin resonance techniques. Several methods were employed for looking at irradiated lead(IV) acetate-carboxylic acid solutions by e.s.r.

#### 3.1 Lead(IV) Acetate Dissolved in Neat Acids

A solution of liquid acids and lead(IV) acetate was prepared by adding excess lead(IV) acetate to the appropriate acid and agitating until no more lead salt would dissolve in the acid. Acids studied in this manner

were valeric, iso-valeric, 2-methylbutyric, vinylacetic, cyclobutanecarboxylic, 2,2-dimethylbutyric, 2,3-dimethyl-2-iso-propylbutyric, neo-heptanoic\* and neo-decanoic\* acids. An inert gas, nitrogen or argon, was bubbled through the solution for 10 minutes and the solution was transferred to either an n.m.r. tube or a 40 mm. o.d. quartz tube previously flushed with the inert gas. The tubes were sealed with a rubber serum stopper and were placed in the room temperature cavity, equipped with a grating on one side through which the sample could be irradiated, of a Varian Electron Spin Resonance Spectrometer. When the spectrum of any of the acids was taken, no signal could be observed. However, when the samples were irradiated with an air-cooled General Electric H100-A4 high pressure mercury vapor lamp, a rather strong singlet was observed from each of the tertiary acids, viz., 2,2-dimethylbutyric acid, neo-heptanoic acid, and neo-decanoic acid. The signal appeared at the same field (H) in each case. No signal was observed on irradiation of any of the other acid solutions. The acids alone showed no signal upon irradiation.

The g-value of this singlet signal from neo-decanoic acid was determined to be 2.0152. The tube containing the acid solution and a tube containing 0.0033% pitch in potassium chloride (supplied with the spectrometer) were placed side by side in the cavity and were irradiated. From the known g-value of pitch, 2.0028, the field (H) at which each signal appeared, and the relationship

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\* These acids were obtained from the Enjay Chemical Co. According to this company's data sheet, neo-heptanoic acid is primarily ( $\sim 95\%$ ) 2,2-dimethylpentanoic acid; the remainder is other 2,2-disubstituted acids. Neo-decanoic acid is only 25% 2,2-dimethyloctanoic acid; the remainder is other tertiary acids.

$$h\nu = g\beta H$$

since  $h\nu$  and  $\beta$  are constant,

$$g_1 H_1 = g_2 H_2$$

or

$$g_1 = \frac{g_2 H_2}{H_1}$$

the  $g$ -value was calculated. Using 1% diphenylpicrylhydrazyl in potassium chloride as the standard ( $g = 2.0030$ ), the  $g$ -value of the signal was again found to be 2.0152.

During irradiation, the intensity of this signal did not change appreciably. However, by successive, rapid sweeps through the signal immediately after extinguishing the light, the intensity of the signal was shown to decrease slowly with time. Upon photolyzing a solution of a tertiary acid, e.g. neo-decanoic acid, and lead(IV) acetate at ambient temperatures and gradually lowering the temperature of the cavity and sample by means of the heat exchanger, successive sweeps showed the signal not to be altered appreciably until the temperature was about  $-30^\circ\text{C}$ . The singlet originally obtained at room temperature was still observed at  $-30^\circ\text{C}$  but it appeared to be broadened with the maximum and minimum of the signal significantly distorted. On lowering the temperature to  $-60^\circ\text{C}$ , the broadening of the signal increased and the maximum and minimum were flattened.

### 3.2 Solutions of Acids and Lead(IV) Acetate

#### 3.2.1 Benzene Solutions

Benzene solutions, 1.5-10 molar in acid and 1 molar in lead(IV) acetate, were prepared with the following acids: phenylacetic, diphenylacetic, triphenylacetic, 2,2-dimethylphenylacetic, 2,2-dimethylbutyric, triethylacetic, and trimethylacetic acids. The solutions were flushed with an inert gas and transferred to tubes as described in 3.1 above. Upon irradiation, only the

three tertiary aliphatic acids., viz. 2,2-dimethylbutyric acid, triethylacetic acid, and trimethylacetic acid, displayed any signal. This signal was a singlet and appeared at the same field as those described in 3.1 above. The signal was shown not to originate from the acid, the benzene, or the lead(IV) acetate alone.

### 3.2.2 Pyridine Solutions

Pyridine solutions, approximately 5 molar in acid and 1 molar in lead(IV) acetate, were prepared using the following acids: cyclobutanecarboxylic acid, 3-cyclohexenecarboxylic acid, vinylacetic acid, endo-2-norbornene-5-carboxylic acid, and 2,2-dimethylbutyric acid. The solutions were treated as previously described (3.2.1). Upon irradiation only the 2,2-dimethylbutyric acid solution showed the singlet signal, previously observed, on sweeping the field. This signal was found to be at a field approximately 10 gauss higher than the signals previously observed. The signal was shown not to originate from the solvent alone, the acid alone, or the lead(IV) acetate alone.

### 3.3 Other Lead(IV) Compounds with Acids

#### 3.3.1 Phenyllead(IV) acetates

Samples of phenyllead triacetate, diphenyllead diacetate, and triphenyllead acetate were separately dissolved in neo-decanoic acid under vacuum. The samples were degassed by freezing in liquid nitrogen under vacuum and thawing with the vacuum released. This procedure was repeated at least twice. After the final thaw, the samples were sealed under vacuum. Upon irradiation of these samples, all displayed the singlet signal on sweeping the field. This signal was not nearly as intense as that described in 3.1 above for neo-decanoic acid and lead(IV) acetate, but appeared at the same field position. Upon extinction of the light, the signal rapidly disappeared (in < 2 minutes, the signal was barely visible), however it grew to its original intensity upon re-irradiation.

### 3.3.2 Solid Lead(IV) Carboxylates

Lead(IV) carboxylates can be prepared<sup>(11)</sup> from lead(IV) acetate and the appropriate acid by dissolving these two components in stoichiometric amounts (1 mole lead(IV) acetate to 4 moles acid) in a solvent, e.g. benzene, and gently heating the solution under vacuum to remove the solvent and the acetic acid liberated by metathesis. The samples used in these studies were prepared in this manner and were recrystallized from benzene or pentane until the lead salt, with the exception of lead(IV) phenylacetate, showed at least > 90% lead(IV) content by iodometric titration.<sup>(3)</sup> Lead(IV) phenylacetate prepared by this manner was a golden yellow in color, whereas all the other lead(IV) carboxylates were very pale yellow. The lead(IV) content of the phenylacetate salt could not be increased beyond 70% by these techniques.

The lead(IV) carboxylates prepared and studied were derived from phenylacetic acid, neo-heptanoic acid, trimethylacetic acid, iso-butyric acid, and n-butyric acid. These solids were placed in quartz tubes and degassed by pumping on the solid with a mercury-diffusion pump apparatus for 1 hr. Upon irradiation in the e.s.r. cavity, the singlet signal previously described was observed with none of the samples.

Irradiation of the lead(IV) trimethylacetate at  $-190^{\circ}\text{C}$  gave a four-line signal. The low field line was the most intense one; the intensity of each line decreased with increasing field. A more well-defined signal could not be obtained by variation of instrument settings. Upon raising the temperature of the irradiated sample to  $-100^{\circ}\text{C}$ , 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  $30^{\circ}\text{C}$ . No signal was observable at room temperature with irradiation. This is definitely not the singlet previously observed and does not appear to be the spectrum

expected to be formed from decarboxylation of the lead(IV) trimethylacetate.<sup>(13)</sup>

### 3.3.3 Solutions of Lead(IV) Carboxylates

The same type of signals were obtained by irradiating solutions of lead(IV) trimethylacetate at  $\sim 100^{\circ}\text{C}$  in the cavity of the spectrometer. Solvents used include benzene, 3:1 ether-toluene (f.p.  $-130^{\circ}\text{C}$ )<sup>(14)</sup>; 1:1 chloroform-toluene; and 14.2:5.8 chloroform-ether (f.p.  $-97.4^{\circ}\text{C}$ )<sup>(14)</sup>.

The lead salt was not appreciably soluble in any of these latter three solvent mixtures, hence the signals obtained were not as intense as with the solid lead salt or with the benzene solution.

These solutions were prepared in the following manner: one ml. of the appropriate solvent was placed in the bottom of a Pyrex test tube attached to a vacuum line by  $\bar{\text{T}}$  joints; a glass tube, attached to the test tube at a slight downward angle and about 2 inches from the bottom of the test tube, contained the lead salt. The solvent was thoroughly out-gassed under vacuum by successive freeze-thaw cycles using liquid nitrogen as the coolant. The full vacuum,  $< 1\mu$  of mercury pressure, was applied to the lead salt at room temperature. The test tube, with attached side tubes, was sealed off under vacuum from the vacuum line. When all components had reached room temperature, the apparatus was rotated so that the lead salt was admixed with the solvent. These components remained together until no more lead salt appeared to dissolve. The liquid was then decanted from the residual lead salt and was allowed to collect in a quartz tube, attached by a quartz to glass graded seal to the test tube and chilled in liquid nitrogen. The quartz tube was then sealed off under vacuum and kept in liquid nitrogen until ready for use for e.s.r. studies.

### 3.4 Outgassed Solutions

a) A benzene solution of lead(IV) trimethylacetate (ca. 0.1M) was prepared as described in Section 3.3.3 using the apparatus shown in Figure 1. A benzene solution of lead(IV) acetate (ca. 0.1M) and trimethylacetic acid (ca. 0.5M) was prepared in a similar manner except that the acid dissolved in the benzene, after degassing by successive freeze-thaw cycles, was added to the solid lead salt. Both of these solutions upon irradiation in the cavity of the e.s.r. spectrometer at  $-100$  to  $-150^{\circ}\text{C}$  displayed the same spectrum as described for solid lead(IV) trimethylacetate in section 3.3.2.

b) A solution similarly prepared from neat neo-dacanoic acid and lead(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 gas (perhaps 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 previously described in section 3.1 was observed.

### 3.5 Observations and Conclusions

Under conditions similar to those described in section 3.4 (a) and (b), Heusler et al.<sup>(13)</sup> reported detecting signals by e.s.r. attributable to alkyl radicals.<sup>(12)</sup> It would be highly speculative to assign the tert-butyl radical as the source of the signals observed under the conditions reported herein. A reasonable source of the signals seen in the spectrum has not yet been ascertained.

Heusler,<sup>(13)</sup> although reporting the alkyl radicals, made no mention of observing any other signals, i.e. signals attributable to the paramagnetic Pb(III) species proposed.<sup>(3,8,9)</sup> Rexroad<sup>(15)</sup> reported

detecting propyl radicals by irradiating tetrapropyl lead at liquid nitrogen temperature (-196°C) with gamma irradiation. He, too, made no mention of signals ascribable to a lead(III) species. In this latter case the decomposition of tetrapropyl lead 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 the inability of workers to observe this intermediate are (1) its absence, or (2) the extremely rapid, even on the e.s.r. 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 lead(III) to be observed.

Since oxygen appears to be necessary for the formation of the species responsible for the sharp singlet described above (3.1), it seems most reasonable that this species is probably a peroxy radical. The g-value herein reported, 2.0152, is within the range (2.0148-2.0155) of g-values found<sup>(12)</sup> for species thought to be alkoxy radicals. The singlet signal was observed<sup>(12)</sup> by irradiation with 2.8meV electrons of various hydrocarbons saturated with air at room temperature. That signals due to peroxy radicals were not observed from secondary and primary acids is probably due (1) to the more difficult decarboxylation of these acids,<sup>(9)</sup> and (2) to the lower stability and more facile decomposition<sup>(16)</sup> of these peroxy radicals.

These results do, however, add further proof for the existence of radicals in the decarboxylation of acids by lead(IV) acetate. Observing radicals in the tertiary acid systems is particularly noteworthy because of the apparent relative ease of oxidation of a tertiary radical to the corresponding cation.

#### 4. Kinetic Studies

In these studies, for each run a stock solution prepared from 11.09 g. (25 mmoles) lead(IV) acetate, 15.0 g. (147 mmoles) trimethylacetic acid and sufficient benzene to give 250 ml. of solution, was prepared. Portions (20 ml.) of the solution were transferred by pipette to each of 12 quartz tubes with total capacity of about 40 ml. After filling the tubes, each one was covered with aluminum foil and the contents were flushed by bubbling an inert gas, nitrogen or argon, through the solution for 10-15 minutes by means of a glass capillary extending to the bottom of the tube. The tubes were stoppered with a securely fastened rubber septum stopper. Tubes were irradiated individually for specific periods of time in duplicate in the Rayonet photochemical reactor using the 3500Å region light for the irradiation. After the irradiation of an individual tube, the contents were poured into a potassium iodide solution, and the liberated iodine was titrated with standardized sodium thiosulfate. Before any solution was photolyzed, the contents of one tube were analyzed by this method. After all solutions were photolyzed, the contents of another unphotolyzed tube were analyzed by the same method to determine if any reaction had occurred during the time required to complete the photolyses. The reaction solutions were stable during the time period required to complete the other photolyses.

Results obtained by this method of analysis were most erratic and irreproducible. For solutions irradiated for exactly the same period of time and treated as nearly alike as possible, variations in the residual lead(IV) in the solution of 10-30% were generally obtained. Numerous attempts to determine the cause of this behavior were unsuccessful: the length of time the inert gas bubbled through the solution was varied, the

photolysis tubes were matched so that the height of the liquid in the tubes for duplicate runs was the same, the samples were photolyzed one at a time rather than the duplicate runs being photolyzed together, and the solutions, protected from room light, were allowed to stand at room temperature prior to photolysis to allow for more complete metathesis of the trimethylacetate for the acetate (from the lead(IV) acetate). The most pronounced effects were noted from the length of time of deaeration and from standing after deaeration before photolysis. Erratic and irreproducible results were still obtained.

##### 5. Quantum Yield Studies

The erratic and irreproducible results encountered in the attempted kinetic studies were also a hindrance in these studies.

The quantum yield, or  $\phi$ , is defined<sup>(17)</sup> as the chemical change in moles divided by the Einsteins absorbed by the solution or

$$\phi = \frac{\text{chemical change in moles of the solution}}{N h \nu \text{ absorbed by the solution}}$$

In these studies uranyl oxalate actinometry was employed. Quartz tubes and the 3500Å lamps in the Rayonet photochemical reactor were used.

The uranyl oxalate was prepared by dissolving 3.782 g. (0.030 mole) oxalic acid dihydrate in 25 ml. warm water and slowly adding a solution of 15.06 g. (0.030 mole) uranyl nitrate hexahydrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) dissolved in warm water. The uranyl oxalate precipitated as the uranyl nitrate solution was slowly added to the stirred oxalic acid solution. After cooling to room temperature the yellow solid was filtered, washed well with distilled water, and dried in a vacuum desiccator. A solution of 0.01 molar in uranyl oxalate and 0.07 molar in oxalic acid was used as the actinometer solution. The titer of this solution was determined with standard 0.1N

potassium permanganate just prior to its use. By irradiating samples of the uranyl oxalate solution for varying periods of time, the change in titer with time of irradiation was shown to be linear. The extinction coefficient of the uranyl oxalate solution (vs. water) was found to be 48.9 at 3500Å, and that of the reaction solution (lead(IV) acetate and trimethylacetic acid in benzene vs. benzene and treated and prepared as in Section 4) 469 at 3500Å.

Using these data and knowing the concentration of the solutions used, the fraction of light absorbed by both solutions could be calculated. By knowing the fraction of light absorbed by both solutions and by determining the quantum efficiency, QE,

where

$$QE = \frac{\text{chemical change in moles}}{Nh\nu \text{ falling on the solution}}$$

the quantum yield of the photolytic decarboxylation of trimethylacetic acid with lead(IV) acetate in benzene could be determined.

The calculated quantum yields varied rather widely, depending on how well the solutions were deaerated. The highest experimentally determined quantum yield was 220.

Even though these determinations were made employing rather crude equipment for actinometric purposes, qualitatively a quantum yield of around 200 is most meaningful. The chain length, the number of molecules reacting per molecule initially decomposed, is at least 200.

## 6. Photolytic Decarboxylation of Acids with Thallium(III) Acetate

The similarities and differences in the oxidative properties of lead(IV) acetate and thallium(III) acetate in various types of reactions of organic compounds have been reported.<sup>(18-21)</sup> Thallium(III) is not as strong an oxidant as is lead(IV).<sup>(18)</sup> Since both are two-electron oxidants, differences in the overall course of the oxidative decarboxylation of acids should be noteworthy in view of the differences in oxidizing properties.

### 6.1 Thallium(III) Acetate

#### 6.1.1 Preparation

The methods of preparation of pure thallium(III) acetate reported in the literature<sup>(18,22,23)</sup> were not desirable because of the poor quality and purity of the product<sup>(18,22)</sup> or because of the inapplicability to large scale production.<sup>(23)</sup>

A procedure was developed for the large scale production of pure (95% Tl(III) or better by titration) thallium(III) acetate in reasonably good yield. The following procedure is exemplary.

Thallium(III) oxide, 457 g. (1 mole), obtained from the American Smelting and Refining Co., New York, New York, was added slowly with stirring to a hot (80-90°) solution of 2 l. glacial acetic acid containing 110 ml. acetic anhydride. After addition was complete, the walls of the flask were washed down with about 500 ml. glacial acetic acid. Stirring and heating (90-100°) were continued until all of the brown oxide had dissolved (about 2 hours). While the solution was still hot, the solution was filtered through a medium sintered glass frit. The filtrate was allowed to cool to room temperature. The precipitate was removed by filtration through a sintered glass frit. The collected solid was dissolved in the smallest possible volume

(about 800 ml.) of glacial acetic acid at 80-90°. The hot solution was again filtered through a sintered glass frit and allowed to cool to room temperature and then to about 15° by cooling in cold water. The thallium(III) acetate was removed by filtration, was spread in a large glass dish, and was placed in a desiccator over solid potassium hydroxide pellets overnight. The material obtained, 467g., 61%, showed a thallium(III) content of 97% (see analysis below).

#### 6.1.2 Analysis

The iodometric analysis for thallium(III) compounds reported<sup>(19,24)</sup> was unsuitable because the end point, even in the presence of starch, was obscured by the intense yellow-orange thallium(I) iodide formed. Excellent analyses were obtained by reducing the thallium(III) with an excess of standardized iron(II) solution (ferrous ammonium sulfate) and titrating the excess iron(II) with a standardized cerium(IV) solution (ceric ammonium sulfate) to the ferrous o-phenanthroline end point.<sup>(25)</sup>

Thallium(I) compounds, organic acids, and solvents were shown not to interfere in the analysis.

#### 6.2 Photolyses

Eleven acids have been studied. Photolyses were conducted with at least duplicate runs at two wavelengths, 2537Å and 3500Å.

##### 6.2.1 General Procedure

Stock solutions were prepared for each duplicate run so that each reaction mixture (20 ml.) contained approximately 2.0 mmoles thallium(III) acetate and approximately 20 mmoles of the appropriate acid. Except where indicated to the contrary, the clear, colorless solutions remained clear and colorless throughout the reaction with no solids precipitating from

solution. Each stock solution was analyzed for thallium(III) content before irradiation and after the reaction was considered over a portion of each reaction solution was analyzed for any unreacted thallium(III).

After a 20 ml. portion of the solution to be photolyzed was placed in a quartz tube, the contents were deaerated as described in Section 4. The tubes were placed in the Rayonet photochamber equipped with lamps to produce light of desired wavelength and were photolyzed for a period of time previously determined to be long enough to ensure complete disappearance of the thallium(III). After the photolysis was completed, the tube was placed in liquid nitrogen to freeze the contents and to condense the gases. The appropriate markers for analysis of the gases were added, and the tubes brought to room temperature with thorough agitation. The gases were analyzed by GC. Pressure was released from the tubes; the contents were removed quantitatively from the tubes and adjusted to a known volume, generally 30 ml., with glacial acetic acid. Aliquots were taken from this diluted solution for analysis of any unreacted thallium(III) and of the remaining products.

#### 6.2.2 Primary Acids

The primary acids employed in this study include n-butyric acid, n-valeric acid, iso-valeric acid, octanoic acid, nonanoic acid, and phenylacetic acid. The 3500Å reaction required approximately 6 times as long as the 2537Å reaction for completion. All acids except phenylacetic acid were redistilled before use.

The products obtained upon photolysis of these acids and thallium(III) acetate in benzene solution at the two wavelengths are shown in Tables IV and V. In all cases the thallium(III) was reduced to thallium(I) and the carbon dioxide yields were near quantitative (that is, 200%) unless otherwise noted.

The products were determined by gas-liquid chromatography using the internal marker method as described in Section 2.1.1 and were compared with authentic samples. The products, the material used as the marker, the GC column and the operating conditions of the GC are given in Table VI.

#### 6.2.3 Secondary Acids

The secondary acids used in this study include isobutyric acid, 2-methylbutyric acid, and cyclohexanecarboxylic acid. The 3500Å reaction took approximately 5 times as long as the 2537Å reaction to reach completion. All acids were redistilled before use. The products obtained upon photolysis of these acids and thallium(III) acetate in benzene solution at the two wavelengths are shown in Table VII. The products were determined as previously described. Table VIII shows the materials analyzed, the markers used in the analysis and the GC column and operating conditions of the GC instrument employed in the analysis. Any materials previously described in Table VI are not included unless either the marker or conditions used was different.

#### 6.2.4 Tertiary Acids

Trimethylacetic acid and 2,2-dimethylbutyric acid were the representatives of tertiary acids studied. The 3500Å reaction took approximately 4 times as long to reach completion as the 2537Å reactions did. Each acid was distilled prior to use. The products obtained after photolysis of these acids and thallium(III) acetate in benzene solution at two wavelengths are listed in Table IX. Unless the marker or conditions used in the analyses were different, these together with the products for which they were used to analyze are shown in Table X.

TABLE IV. Products Obtained from the Photolysis of Primary Acids with Thallium(III) Acetate in Benzene Solution at Two Wavelengths<sup>a</sup>

Acid	% Methane	% Alkane	% Alkene	% Dimer	% Acetate Ester	% Higher Ester	% Alkyl benzene	% Other
<u>At 2537Å</u>								
n-butyric	3.3	34 <sup>b</sup>	10 <sup>c</sup>	30 <sup>d</sup>	n.d.	1.3 <sup>e</sup>	1.1 <sup>f</sup>	4 <sup>g</sup>
n-valeric	3.5	31 <sup>g</sup>	10 <sup>h</sup>	33 <sup>i</sup>	1.4 <sup>j</sup>	5.1 <sup>k</sup>	.8 <sup>l</sup>	
iso-valeric	2.7	26 <sup>m</sup>	7.1 <sup>n</sup>	38 <sup>o</sup>	n.d.	0.6 <sup>p</sup>	1.6 <sup>q</sup>	5 <sup>r</sup>
phenyl-acetic <sup>y</sup>	1.6	16 <sup>s</sup>	-	49 <sup>t</sup>	2.4 <sup>u</sup>	14 <sup>v</sup>	0.7 <sup>w</sup>	0.4 <sup>x</sup>
<u>At 3500Å</u>								
n-butyric	4.7	96 <sup>b</sup>	1.7 <sup>c</sup>	5.3 <sup>d</sup>	n.d.	6.1 <sup>e</sup>	1.4 <sup>f</sup>	
n-valeric	4.8	69 <sup>g</sup>	1.2 <sup>h</sup>	7.1 <sup>i</sup>	1.5 <sup>j</sup>	3.3 <sup>k</sup>	6.0 <sup>l</sup>	
iso-valeric	3.6	59 <sup>m</sup>	1.8 <sup>n</sup>	7.5 <sup>o</sup>	n.d.	0.6 <sup>p</sup>	4.4 <sup>q</sup>	
phenyl-acetic <sup>z</sup>	4.1	30 <sup>s</sup>		41 <sup>t</sup>	2.4 <sup>u</sup>	23 <sup>v</sup>	1.4 <sup>w</sup>	

(a) Percentages are expressed as moles of product per mole of thallium(III) reacted; (b) Propane; (c) Propene; (d) Hexane; (e) Propyl butyrate; (f) Propylbenzene; (g) Butane; (h) Butene-1; (i) Octane; (j) n-Butyl acetate; (k) n-Butyl valerate; (l) n-Butylbenzene; (m) iso-Butane; (n) iso-Butene; (o) 2,5-dimethylhexane; (p) iso-Butyl iso-valerate; (q) iso-Butylbenzene; (r) 2-Methylbutane; (s) Toluene; (t) Bibenzyl; (u) Benzyl acetate; (v) Benzyl phenylacetate; (w) Diphenylmethane; (x) Ethylbenzene; (y) Approximately 290% carbon dioxide formed; (z) Carbon dioxide yield near 200%.

TABLE V. Hydrocarbons Obtained from the Photolysis of Octanoic Acid and Nonanoic Acid with Thallium(III) Acetate in Benzene Solution at Two Wavelengths<sup>a</sup>

Acid	Wavelength	% Methane	% Alkane	% Alkene	% Dimer
Octanoic	2537Å	6.2	22 <sup>b</sup>	9.2 <sup>c</sup>	18 <sup>d</sup>
Nonanoic	2537Å	7.0	22 <sup>e</sup>	4.6 <sup>f</sup>	21 <sup>g</sup>
Octanoic	3500Å	6.8	52 <sup>b</sup>	n.d.	
Nonanoic	3500Å	6.9	48 <sup>e</sup>	3.4 <sup>f</sup>	

(a) Percentages are expressed as moles of product per mole of thallium(III) reacted; numerous unidentifiable products were produced in addition to those reported here; (b) Heptane; (c) Heptene-1 and cis and trans heptene-2, complete separation could not be achieved; (d) Tetradecane; (e) Octane; (f) Octene-1 and cis- and trans-octene-2, complete separation could not be achieved; (g) Hexadecane.

TABLE VI. Markers and Conditions Used in Determining Yields of Products from Primary Acids

Material Analyzed	Marker Used	GC Column and Conditions
Methane	Ethane	12 ft. silica gel, room temperature
Carbon dioxide	Ethane	12 ft. silica gel, room temperature
Propane	Isobutane	15 ft. 30% Dowtherm on Firebrick, 15°C.
Propene	Isobutane	15 ft. 30% Dowtherm on Firebrick, 15°C.
n-Butane	Isobutane	15 ft. 30% Dowtherm on Firebrick, room temp.
Butene-1	Isobutane	15 ft. 30% Dowtherm on Firebrick, room temp.
Isobutane	n-Butane	" " " " " " "
Isobutene	n-Butane	" " " " " " "
Hexane	Octane	8 meter 20% DEGS on Chromosorb W, 70°
n-Propylbutyrate	sec-Butylbenzene	9 ft. 20% DEGS on acid washed firebrick
n-Propylbenzene	sec-Butylbenzene	" " " " " " "
n-Octane	n-Heptane	12 ft. 15% didecylphthalate, 5% Bentone 34 on Chromosorb W, 90°C.
n-Butyl acetate	iso-Butyl acetate	" " " " " "

TABLE VI (cont.)

Material Analyzed	Marker Used	GC Column and Conditions
n-Butyl valerate	Ethyl-hexanoate	9 ft. 20% DEGS on acid washed firebrick, 104°
n-Butylbenzene	iso-Propylbenzene	" " " " "
2,5-Dimethylhexane	n-Octane	8 ft. 20% SF-96 on Chromosorb W, HMDS, 67°
iso-Butyl iso-valerate	n-Butylbenzene	9 ft. 20% DEGS on acid washed firebrick, 104°
iso-Butylbenzene	n-Butylbenzene	" " " " "
2-Methylbutane	n-Butane	15 Ft. 30% Dowtherm on firebrick, room temp.
Toluene	Ethylbenzene	12 ft. 15% didecylphthalate, 5% Bentone 34 on Chromosorb W, 120°
Ethylbenzene	Toluene	" " " " "
Dibenzyl	Dicyclohexyl	6 ft. 20% SF-96 on Chromosorb W, HMDS, 150°
Diphenylmethane	Dicyclohexyl	" " " " " "
Benzyl acetate	"	" " " " " "
Benzyl phenylacetate	Phenyl benzoate	" " " " " "

TABLE VII. Products Obtained from the Photolysis of Secondary Acids with Thallium(III) Acetate in Benzene Solution at Two Wavelengths<sup>a</sup>

Acid	% Methane	% Alkane	% Alkene	% Dimer	% Acetate ester	% Higher ester	% Alkyl-benzene	% Other
<b>At 2537Å</b>								
iso-Butyric	4.6	52 <sup>b</sup>	50 <sup>c</sup>	16 <sup>d</sup>	n.d.	n.d.	0.9 <sup>e</sup>	2 <sup>f</sup>
2-Methyl-butyrlic	2.9	35 <sup>g</sup>	25 <sup>h</sup> 11 <sup>i</sup> 9.5 <sup>j</sup>	19 <sup>k</sup>	n.d.	1.3 <sup>l</sup>	0.8 <sup>m</sup>	3 <sup>n</sup>
Cyclohexane-carboxylic	4.8	27 <sup>o</sup>	17 <sup>p</sup>	7.6 <sup>q</sup>	1.7 <sup>r</sup>	6.9 <sup>s</sup>	.8 <sup>t</sup>	0.2 <sup>u</sup>
<b>At 3500Å</b>								
iso-Butyric	3.2	84 <sup>b</sup>	26 <sup>c</sup>	3.2 <sup>d</sup>	n.d.	n.d.	3.6 <sup>e</sup>	
2-Methyl-butyrlic	4.9	49 <sup>g</sup>	11 <sup>h</sup> 6.9 <sup>i</sup> 6.2 <sup>j</sup>	5.6 <sup>k</sup>	n.d.	1.7 <sup>l</sup>	3.6 <sup>m</sup>	
Cyclohexane-carboxylic	2.6	48 <sup>o</sup>	13 <sup>p</sup>	2.8 <sup>q</sup>	1.6 <sup>r</sup>	5.8 <sup>s</sup>	2.2 <sup>t</sup>	

(a) Percentages are expressed as moles of product per mole of thallium(III) reacted; (b) Propane; (c) Propene; (d) 2,3-Dimethylbutane-1; (e) iso-Propylbenzene; (f) iso-Butane; (g) n-Butane; (h) Butene-1; (i) trans-2-butene; (j) cis-2-butene; (k) 3,4-Dimethylhexane; (l) sec-Butyl 2-Methylbutyrate; (m) sec-Butylbenzene; (n) 2-Methylbutane; (o) Cyclohexane; (p) Cyclohexene; (q) Dicyclohexyl; (r) Cyclohexyl acetate; (s) Cyclohexyl cyclohexanecarboxylate; (t) Cyclohexylbenzene; (u) Methylcyclohexane.

TABLE VIII. Markers and Conditions Used in Determining Yields of Products from Secondary Acids

Material Analyzed	Marker Used	GC Column and Conditions
Propane	n-Butane	15 ft. 30% Dowtherm on fire-brick, 15°
Propene	n-Butane	Same as above
Isobutane	n-Butane	Same as above
2,3-Dimethylbutane	n-Octane	8 meter, 20% DEGS on Chromosorb W, 70°C.
iso-Propylbenzene	sec-Butylbenzene	9 ft. 20% DEGS on acid washed firebrick, 71°C.
n-Butane	iso-Butane	15 ft. 30% Dowtherm on fire-brick, room temperature
Butene-1	iso-Butane	Same as above
trans-2-Butene	iso-Butane	Same as above
cis-2-Butene	iso-Butane	Same as above
2-Methylbutane	iso-Butane	Same as above
3,4-Dimethylhexane	n-Octane	8 ft. 20% SF-96 on Chromosorb W, HMDS, 67°C.
sec-Butyl-2-methylbutyrate	n-Butylbenzene	9 ft. 20% DEGS on acid washed firebrick, 71°
sec-Butylbenzene	n-Butylbenzene	Same as above
Cyclohexane	n-Hexane	8 meter 20% DEGS on Chromosorb W, 55°C.
Cyclohexene	n-Hexane	Same as above
Methylcyclohexane	n-Hexane	Same as above
Dicyclohexyl	n-Amylbenzene	6 ft. 5% triisodecyl trimellitate, 5% Bentone 34 on Chromosorb P, HMDS, 125°.
Cyclohexylacetate	n-Amylbenzene	Same as above
Cyclohexylbenzene	n-Amylbenzene	Same as above
Cyclohexyl cyclohexanecarboxylate	n-Heptyl cyclohexanecarboxylate	4 ft. 20% SF-96 on Chromosorb W, HMDS, 170°C.

TABLE IX. Products Obtained from the Photolysis of Tertiary Acids with Thallium(III) Acetate in Benzene Solution at Two wavelengths<sup>a</sup>

Acid	% Methane	% Alkane	% Alkene	% Dimer	% Acetate Ester	% Higher Ester	% Alkylbenzene
<u>At 2537Å</u>							
Trimethylacetic	4.6	33 <sup>b</sup>	55 <sup>c</sup>	6.4 <sup>d</sup>	3.5 <sup>e</sup>	3.3 <sup>f</sup>	0.2 <sup>g</sup>
2,2-Dimethylbutyric	n.d.	43 <sup>h</sup>	45 <sup>i</sup> 18 <sup>j</sup>	6.0 <sup>k</sup>	0.5 <sup>l</sup>	1.4 <sup>m</sup>	1.5 <sup>n</sup>
<u>At 3500Å</u>							
Trimethylacetic	0.6	29 <sup>b</sup>	36 <sup>c</sup>	3.9 <sup>d</sup>	10	8.2	n.d.
2,2-Dimethylbutyric	n.d.	35 <sup>h</sup>	35 <sup>i</sup> 19 <sup>j</sup>	4.2 <sup>k</sup>	1.8 <sup>l</sup>	2.8 <sup>m</sup>	1.1 <sup>n</sup>

(a) Percentages are expressed as moles of product per mole of thallium(III) reacted; (b) iso-Butane; (c) iso-Butene; (d) 2,2,3,3-tetramethylbutane; (e) t-Butylacetate; (f) t-Butyltrimethylacetate; (g) t-Butylbenzene; (h) 2-Methylbutane; (i) 2-Methyl-1-butene; (j) 2-Methyl-2-butene; (k) 3,3,4,4-Tetramethylhexane; (l) t-Amylacetate; (m) t-Amyl-2,2-dimethylbutyrate; (n) t-Amylbenzene.

TABLE X. Markers and Conditions Used in Determining Yields of Products from Tertiary Acids

Material Analyzed	Marker Used	GC Column and Conditions
iso-Butane	n-Butane	15 ft. 30% Dowtherm on firebrick, room temperature
iso-Butene	n-Butane	Same as above
2,2,3,3-Tetramethyl-butane	n-Butyl acetate	12 ft. 20% SF-96 on Chromosorb W, HMDS, 90°C.
tert-Butyl acetate	n-Butyl acetate	Same as above
tert-Butyl trimethyl-acetate	n-Butyl acetate	Same as above
tert-Butylbenzene	n-Butyl acetate	7 ft. 20% SF-96 on Chromosorb W, HMDS, 120°C.
2-Methylbutane	n-Pentane	10 ft. 30% Dowtherm on firebrick, 42°C
2-Methyl-1-butene	n-Pentane	Same as above
2-Methyl-2-butene	n-Pentane	Same as above
tert-Amyl acetate	Cyclohexyl acetate	12 ft. 20% SF-96 on Chromsorb W, HMDS, 165°C.
3,3,4,4-Tetramethyl-hexane	Cyclohexyl acetate	Same as above
tert-Amylbenzene	Cyclohexyl acetate	Same as above
tert-Amyl-2,2-di-methylbutyrate	Cyclohexyl acetate	Same as above

### 6.3 Observations and Conclusions

Investigation of Table IV reveals some most interesting differences in the products formed during the photolysis of primary acids. The shorter wavelength irradiation, 2537Å, produces greater amounts of alkene and dimer than does the 3500Å reaction. Most significant in the 2537Å reaction, however, is the formation of products, e.g. butane from n-butyric acid and pentane from n-valeric acid, which may be pictured as originating from the coupling of a methyl radical and the radical produced from the decarboxylation of the acid. Also noteworthy is the relatively small quantities of esters and alkylbenzenes formed at both of these wavelengths. The alkene/dimer ratio in each example, except phenylacetic acid from which no alkene is possible, is approximately 0.3. This is close to the ratio (0.4) of these products formed in the vapor phase disproportionation-recombination of primary radicals.<sup>(26)</sup> Although photolytic reactions in solution and thermal gas phase reactions probably are highly dissimilar, the proximity of these ratios is quite striking.

The amounts of alkene and dimer formed in the 2537Å reaction in both the secondary acid and tertiary acid photolyses are seen also to be greater than in the 3500Å reaction, as seen from Tables VII and IX. Even in the case of tertiary acids, relatively small quantities of acetates and alkylbenzenes are formed. Even the alkene yields in the tertiary cases are not significantly greater than in the secondary cases. This points to the apparent inefficiency of alkyl radical, be it primary, secondary or tertiary, oxidation by thallium(III).

Upon examination of the primary, secondary, and tertiary acid series, with the exception of the two butyric acids and phenylacetic acid, the alkanes at 2537Å and the alkenes at both wavelengths show a general increase upon going from primary to secondary to tertiary acids; the alkanes at 3500Å and

the dimers at both wavelengths show a general decrease in this same sequence of acid structure.

That substantial quantities of dimers are formed even with tertiary acids and that relatively low yields of products of oxidation (except alkenes) are formed in all cases, points to the largely radical nature of the reaction. It may even be proposed that a cage reaction is predominant, at least with the primary acids at  $2537\text{\AA}$ , in view of the apparent disproportionation-recombination ratio observed. Since the light of shorter wavelength is more energetic, the radicals produced might be expected to be more energetic and react indiscriminantly with whatever entity may be near it.

The derivation of the two butyric acids from the seeming trends established by the other acids is unexplainable.

Of all the acids studied and reported here, the photolysis of phenylacetic acid at  $2537\text{\AA}$  is the only case in which the thallium(III) appeared to be reduced to the metal. The 300% yield of carbon dioxide bears this out. No explanation for this anomaly has yet been conceived. Other instances of the anomalous behavior of reactions of phenylacetic acid have been observed.<sup>(10)</sup>

#### 6.4 Photolyses Conducted in Hydrogen-donor Solvents

In order to determine if the photolysis at  $2537\text{\AA}$  of primary acids and thallium(III) acetate in benzene solution does indeed involve radical cage reactions, photolyses at this wavelength were conducted using various amounts of hydrogen-donor compounds, e.g., cumene, diphenylether, and chloroform, as part of the solvent system. Copper(II), known<sup>(9)</sup> to be a particularly effective oxidant of alkyl radicals produced in lead(IV) acetate decarboxylations, was also employed as a radical trap. Valeric acid was used in these studies. The solutions for photolysis were prepared as before except that the appropriate hydrogen donor (previously distilled under

nitrogen and stored under nitrogen in the freezer) was added to the solution prior to bubbling the inert gas through the solution. When copper(II) acetate was used, this salt was first dissolved in the valeric acid and then the remaining components of the reaction solution were added to this solution.

The yields of only the hydrocarbon products, alkane, alkene, and dimer, and carbon dioxide were determined since these were the products necessary for the verification of the cage reaction theory. The variation of these products with the amount of hydrogen donor and copper(II) acetate added is shown in Table XI.

Of the radical traps employed, the effect of copper(II) is the most readily understood. Whereas in the copper(II) catalyzed thermal decarboxylation of valeric acid with lead(IV) acetate, butene-1 is practically the sole product,<sup>(9)</sup> in the photolytic (2537Å) decarboxylation employing thallium(III) acetate significant quantities of butane and octane are formed even when the Cu(II) to Tl(III) ratio is 1:2. This implies that radicals, once produced in this reaction, react essentially instantaneously with whatever is available since copper(II) reacts with butyl radicals at a rate approaching one diffusion controlled. With copper(II) in chloroform solution, the chloroform is more successful at reacting with the radical than is the copper.

With cumene present, the amount of butane formed is greater than that formed in the absence of cumene. The diminution of all products with increasing cumene concentration, except butane with cumene as the solvent, may be explained by assuming that some of the thallium is reacting with cumene, or radicals derived from it by hydrogen abstraction (i.e., the cumyl radical), rather than all of it undergoing the decarboxylation reaction exclusively.

TABLE XI. The Variation of Butane, Butene-1, and Octane Yields with Radical Tray Concentration

Radical Trap Concentration	% Butane	% Butene-1	% Octane	% Carbon Dioxide <sup>a</sup>
$\frac{\text{moles cumene}}{\text{moles initial Tl(III)}} = 1$	42.4	12	32.3	200
$\frac{\text{moles cumene}}{\text{moles initial Tl(III)}} = 12$	40.3	10	27.8	207
$\frac{\text{moles cumene}}{\text{moles initial Tl(III)}} = 37$	39.8	7.9	17.7	174
cumene as solvent	44.6	6.1	11.4	154
$\frac{\text{moles dibenzyl ether}}{\text{moles initial Tl(III)}} = 1$	33.5	7.4	26.2	193
$\frac{\text{moles dibenzyl ether}}{\text{moles initial Tl(III)}} = 11$	53.2	2.4	6.6	107
dibenzyl ether as solvent	35.2	0	0.3	46
$\frac{\text{moles chloroform}}{\text{moles initial Tl(III)}} = 1$	46.5	8.5	n.d.	206
$\frac{\text{moles chloroform}}{\text{moles initial Tl(III)}} = 9.4$	100	5.2	10.6	239
chloroform as solvent	205	0	3.2	276
5.3 mole % Cu(II)	10	81.7	3.4	150
50 mole % Cu(II)	7.2	86.9	3.0	n.d.
4.6 mole % Cu(II) with chloroform solvent	132	3.0	2.7	233
none	31	10	33	200

(a) Yields of carbon dioxide were determined using an 8 ft. Porapak Q column at 65°C. with ethane as the marker. These analyses are perhaps more reliable than those performed using the silica gel column; the carbon dioxide peak observed using the silica gel suffered from rather severe post-tailing.

(Small amounts of  $\alpha$ -methylstyrene were observed but not determined quantitatively.) This appears to be occurring in the dibenzyl ether instances, also. With dibenzyl ether as the solvent, the solution is quite viscous. If a cage reaction were to take place, it should be evinced here. However, decarboxylation appears to be the minor reaction in this case as is indicated by the very small carbon dioxide yield.

Chloroform is perhaps the best hydrogen donor of the compounds studied. Increasing the chloroform concentration greatly enhances the butane formation. However, with large quantities of chloroform present, the thallium is reduced to the metal. No plausible explanation for this phenomenon has yet been found.

It is noteworthy that in cases where butene-1 is not found (with both dibenzyl ether and chloroform as solvents), the radicals appear to react with themselves (dimerization) or with the solvent, with the latter much more prevalent.

#### 6.5 Attempts at Effecting the Thermal Decarboxylation with Thallium(III)

Several attempts were made to effect the thermal decarboxylation of trimethylacetic acid with thallium(III) acetate. The solutions were prepared as described in Section 2.1.1. Even with sodium acetate, pyridine, or copper(II) acetate, materials known to catalyze the decarboxylation<sup>(9,10)</sup> with lead(IV) acetate, added to the refluxing benzene solutions, up to 50% of the initial thallium(III) was present after one week of reaction.

#### 6.6 Conclusions

The decarboxylation of acids with thallium(III) acetate has been found to proceed only photolytically, for all practical purposes. The structure of the acids does not determine the course of the reaction to a profound degree. Radical reactions can account for a large portion of the

products be they derived from primary, secondary, or tertiary acids. The radicals, once they are generated, appear to react indiscriminately with whatever is most readily available. Much is known about the reaction, but to propose a mechanism is not yet possible.

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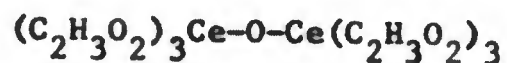
### PART III. SYNTHESIS AND CHARACTERIZATION OF CERIC ACETATE

#### 1. Introduction

The usual method of preparation of lanthanide acetates is to heat the oxide or the carbonate with the appropriate acid. The preparation of anhydrous acetates has posed a difficult problem, however. One method that has worked for at least neodymium and samarium has been to simply react the oxide with acetic anhydride.<sup>(1)</sup> An earlier method of reacting the oxide with fused ammonium acetate gave impure products. In 1960 Moeller, Galasyn and Xavier reported a method of dehydrating rare earth metal acetates by treatment with N,N-dimethylformamide and benzene, followed by azeotropic distillation.<sup>(2)</sup> When DMF solvated acetates were obtained the anhydrous forms were easily prepared by heating in vacuo above 200°. Several groups reported efforts to prepare anhydrous acetates from the reaction between hydrated nitrates and acetic anhydride, but they apparently found that they obtained oxyacetates rather than acetates.

Although cerous acetate has been known for some years, anhydrous ceric acetate was not reported until 1956. Job had reported in 1903 that an aqueous solution of cerous acetate was oxidized to ceric acetate by ozone. He also reported that basic ceric acetate,  $Ce(OAc)_3OH$ , was prepared by boiling a solution of a ceric salt with excess of an alkali acetate.<sup>(3)</sup> In 1956 Patnaik and Panda reported the preparation of anhydrous ceric acetate by reacting cerous nitrate with a mixture of glacial acetic acid and acetic anhydride.<sup>(4)</sup> They found the compound to be garnet-red in the crystalline state and lemon-yellow in the powder. They found that the compound was extremely sensitive to water, turning white upon contact. They reported that the compound was light-sensitive, being reduced to the cerous state upon exposure in the absence of moisture. They also found that in the absence of light and moisture the thermal decomposition maintained the ceric state. At 65° they reported the primary

decomposition product was diceric mono-oxy hexa-acetate:



The primary product at 100° was of empirical formula  $\text{CeC}(\text{C}_2\text{H}_3\text{O}_2)_2^5$  Patnaik and Panda were undecided between two possible structures:



Ceric acetate appeared to be a good choice for a metal carboxylate that would undergo a one-electron reduction decarboxylation. The purpose of the recent and continuing effort has been to prepare and identify ceric acetate.

## 2. Experimental

Initial experimental efforts were an attempt to prepare ceric acetate directly from ceric salts by refluxing with acetic acid-acetic anhydride mixtures. These experiments were first performed in flasks covered with aluminum foil and fitted with a reflux condenser stoppered with a calcium chloride drying tube. They were repeated in the dark under a dry nitrogen atmosphere in a glove box. The procedure was to reflux a dried sample of about .005 mole of the ceric salt in 72 ml. of an acetic acid-acetic anhydride solution prepared by refluxing 55 ml. of glacial acetic acid (Baker and Adamson, Allied Chemical) with 17 ml. of acetic anhydride (Fisher Certified, distilled at 132-135°C) for thirty minutes. The samples were dried in a vacuum dessicator at room temperature over calcium chloride and potassium hydroxide for 48 hours. The cerium salts employed were:

- 1) Ceric sulfate  $\text{Ce}(\text{SO}_4)_2$  (American Potash and Chemical Corporation, Code 291, lot 1118, Lindsay Rare Earth Chemicals, West Chicago, Ill.)
- 2) Ceric oxide  $\text{CeO}_2$  (G. Frederick Smith Chemical Company, Columbus, Ohio)
- 3) Ceric ammonium sulfate  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$  (G. Frederick Smith Chemical Company, Columbus, Ohio)
- 4) Cerous chloride  $\text{CeCl}_3 \cdot x\text{H}_2\text{O}$  (American Potash and Chemical Corporation, Code 237, lot U1108, Lindsay Rare Earth Chemicals, West Chicago, Illinois)

The ceric sulfate and ceric ammonium sulfate were analyzed for ceric content by dissolving a carefully weighed dried sample in a known volume of dilute sulfuric acid, adding an excess of standard ferrous ammonium sulfate solution and two drops of ferrous-ortho-phenanthroline indicator solution, and back titrating with standard ceric ammonium sulfate to the color change. In most cases a few drops of phosphoric acid were added to sharpen the end point. The ferrous solution was prepared by placing about 40 grams of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (J. T. Baker Chemical Company, Phillipsburg, N. J.) in a one liter volumetric flask and diluting to the mark with 20 ml. of sulfuric acid and distilled water. The standard ceric solution was prepared by the general procedure:

    Weigh out .64-.66 gm. of ceric ammonium sulfate into a solution of 28 ml. of concentrated sulfuric acid in 500 ml. of water, stir until complete solution is effected, and dilute to one liter.

The solution was standardized against arsenic trioxide (Mallinckrodt Chemical Works, St. Louis, Missouri,  $\text{As}_2\text{O}_3$  assay 99.95-100.05%, Analytical Reagent-Primary Standard Quality, About .25 gram of arsenic trioxide was dried for two hours at  $110^\circ\text{C}$ , and was then weighed into a flask. The solid was dissolved in 20 ml. of 5% sodium hydroxide solution, and then 100 ml. of distilled water was added, followed by 25 ml. of 1:5 sulfuric acid. Three drops of .01M osmium tetroxide solution was added, followed by a few drops of ferrous-ortho-phenanthroline indicator solution. This

solution was then titrated with the ceric solution to the first sharp color change.

The ceric oxide was analyzed by dissolving .67-.68 gram of the oxide in a solution of 2 grams of potassium iodide in excess HCl. The iodine was titrated with thiosulfate:



The cerous salt was not analyzed.

All of the salts proved to be nearly insoluble, even after several days of stirring and heating. The ceric salts appeared to be slowly reduced. The ceric sulfate and ceric ammonium sulfate turned beige within 24 hours, while no visible change occurred in the cerous chloride or ceric oxide. Only a few per cent of the original ceric titer was observed in any case after 24 hours. Trials were performed in closed systems to permit collection of any gasses in a water filled, inverted cylinder, but no gas was collected.

The next approach to the synthesis of ceric acetate was to ozonize acetic acid-acetic anhydride solutions or suspensions of cerous acetate and cerous carbonate. It was found that a solution of cerous acetate about .2-.3 molar in acetic acid-acetic anhydride thickened within a short time and became solid. This process usually took only about a minute, but the time varied from a few seconds to several minutes depending upon concentration, etc. The solid, probably a cerous acetate polymer, was collected and dried and was found to have a melting point in excess of 250°C. It was barely soluble in dilute sulfuric, and the very crude titrations permitted showed no ceric content. The first problem in the ozonation, then, was to find complexing agents to prevent the formation

of the solid. Some of the more effective agents for this purpose were HF, H<sub>2</sub>SO<sub>4</sub>, organic bases such as pyridine and t-butylamine, all used in very small quantities. The best solvent was 3:1 by volume dimethylsulfoxide and acetic acid. Sulfolane was also used. The results were inconclusive, but the intensity of color obtained with ozonation did not appear to be as intense as with DMSO.\*

The ozonations were performed in flasks fitted with gas dispersion tubes, using a .1 molar aqueous KI trap. The ozone was produced by running dry oxygen through a Welsbach Ozonator, Model T-816. An exact determination of the ozone production of the machine, requiring the use of a wet test meter, was not made, but a good approximate calibration was made using the flow gauges on the machine. Those gauges were calibrated to read standard cubic feet per minute at 8.0 pounds per square inch oxygen pressure and 70°C. The ozone-oxygen mixture produced by the ozonator was passed through an acetic acid-acetic anhydride solution like that used in the preparative trials and then into the KI trap. The liberated iodine was titrated with sodium thiosulfate solution that had been standardized with KIO<sub>3</sub>. The method of standardizing the thiosulfate



was to weigh out .14-.15 gm. of dried (120° for several hours) potassium iodate (J. T. Baker Chemical Company, Phillipsburg, N. J.). This was then

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\* The sulfolane was purified by distilling 4 times over KOH under vacuum until the addition of H<sub>2</sub>SO<sub>4</sub> produced very little color change. The liquid was then vacuum distilled over calcium hydride. The final sample was colorless and nearly odorless. The sulfolane was produced by Shell Oil Company.

The DMSO, both Matheson and Crown Zellerbach, contained impurities giving it a dark red-orange color. The colored material precipitated upon heating. The DMSO was distilled over calcium hydride at about 2 cm. Hg pressure and about 78-82°C.

dissolved in 25 ml. of cold boiled-out distilled water, and 2 grams of KI and 5 ml. of 2N H<sub>2</sub>SO<sub>4</sub> were added. The liberated iodine was titrated with the sodium thiosulfate solution until the liquid was pale yellow. It was then diluted to about 200 ml. with distilled water, 2 ml. of starch solution was added, and the titration was continued until the blue to colorless end point.



It was found that O<sub>3</sub> production per unit time increased linearly with flow rate and with relative pressure of the oxygen. O<sub>3</sub> production varied almost linearly with voltage at low values and approached a maximum asymptotically at about 130 volts. Using thiosulfate solution standardized at .1045N ± .0002N (three trials) and at the most frequently used setting of flow rate = .035 cfm, pressure (relative) = 7.0 psi, 120 volts, 155-160 watts, three five-minute blanks required 68.90 ml. of thiosulfate, 73.80 ml., and 59.00 ml. These gave O<sub>3</sub> production rates per 5 minutes of .003600 mole, .003856 mole, and .003083 mole. No effort was made to find ways to improve the amount of variation in the output.

In a typical trial with cerous acetate (3.7602 gm., G. F. Smith Chemical Company, Columbus, Ohio) in 100 ml. of acetic acid-acetic anhydride containing a few drops of HF, about .0025 mole of O<sub>3</sub> passed through the trap, indicating that some O<sub>3</sub> was being absorbed by the cerous acetate, but perhaps as little as .0005 mole per 5 minutes for the roughly .01 mole of cerous.<sup>6</sup> The yellow solutions that were obtained upon ozonation were rotary evaporated to yield a dark red-brown solid which was yellow when dried and had a very low ceric titer. The yellow solution produced in one of the trials using DMSO-acetic acid as solvent

lost its color with the evolution of gas when exposed to sunlight for about  $1\frac{1}{2}$  hours.

The many trials of ozonating solutions of cerous acetate and cerous carbonate had produced little of satisfaction when, by chance, cerous carbonate (G. F. Smith Chemical Company, Columbus, Ohio) and cerous acetate were obtained from the Smith Company that contained nitrate impurities. Both had been prepared from the nitrate. The mixtures turned yellow upon heating, and as complete solution was effected the solutions turned very dark brown and evolved a gas having the appearance and odor of  $\text{NO}_2$ . The complete solutions were stable for several hours, and when they were ozonated for an hour they produced a massive yellow precipitate which was collected by suction filtration, washed with acetic acid-acetic anhydride and dried in a vacuum desiccator for several days. It was found that the addition of a small amount of nitric acid seemed to increase the rate of solution but had no effect upon the yield. The product appeared to have a negative temperature coefficient of solubility, and heating the solution to  $55-60^\circ$  before filtering increased the yield. The ozonation was apparently exothermic because the gas entering the flask was close to room temperature while the flask heated to about  $55^\circ$  during the ozonation. It was also noted that if the reaction mixture was not refluxed until  $\text{NO}_2$  evolution ceased before ozonation, the product was very difficult to precipitate.

Before analyzing the product some effort was directed toward perfecting persulfate oxidations of cerous to ceric. The following method gave consistent results for cerous acetate supplied by Lindsay Potash and Chemical Company (99.9%):

Place the cerous salt (usually .25-.50 gram) in a few ml. (about 10) of concentrated sulfuric acid and heat with a burner almost to dryness. Take the dark brown residue up into about 50 ml. of a dilute solution of sulfuric acid and ammonium sulfate. Add 5 ml. of .1M silver nitrate solution and 10 ml. of saturated ammonium persulfate. Heat ten minutes on a water bath and then boil at least 10 minutes to destroy the excess persulfate. Titrate with ferrous and ceric after allowing to cool to room temperature.

It was found that the length of time of drying and exposure to atmospheric air before treatment and weighing changed the results of the titrations slightly. The results varied from 93.8% cerous acetate by weight to 95.3%. The mole weight of cerous acetate is 317.26 in the anhydrous form and 344.28 with  $1\frac{1}{2}$  waters of hydration. A blank was not run to determine if any persulfate remained. However, the results did not vary in any uniform manner when the solutions were boiled for 10 minutes or longer.

The exact yield with Lindsay cerous acetate was not yet determined. With Smith cerous acetate that had not been analyzed two typical trials gave yields of 73.4% and 75.9% of theoretical, assuming pure starting materials. No effort was made to increase the yield by concentrating the solution, and it was brightly colored. The observed yields of 75-80% were lower than the best possible then. The yields were calculated assuming that the product was ceric acetate. In the first case 20.1411 gm. of Smith cerous acetate had been added to a solution of 100 ml. of glacial acetic acid and 34 ml. of acetic anhydride (Fisher Certified, distilled 132-135°). The solution was ozonated for one hour under the usual conditions, and the product was dried for 24 hours in the vacuum desiccator before weighing. Its mass was 17.5 gm. Assuming pure dry cerous acetate (FW 317) and pure dry ceric acetate (FW 376) .0466 mole of product was obtained from .0635 mole of starting material.

The ceric analysis was performed on the product by first dissolving the product (.01-.3 gm.) in a few ml. of concentrated sulfuric acid to the greatest possible extent. A few ml. of distilled water were then added quickly with fast stirring, and when complete solution was effected the solution was diluted to 200-300 ml. with distilled water. Excess ferrous was added, and the solution was back-titrated with ceric in the usual manner. It was found that the length of drying time, the number of recrystallizations, and other less controllable factors made a considerable difference in the mole weight found per ceric by the ceric-ferrous titration. This was probably due to varying amounts of acetate associated with the ceric ion. It was found that several days of drying were required before the product no longer lost weight and had no odor. In one trial .7861 gm. of the product, which had been dried 10 days to constant weight, was neutralized with 21.0 ml. of ferrous solution and back-titrated with 4.6 ml. of ceric solution. The ceric solution had been standardized as  $.0994 \pm .0002M$ ; the ferrous titer was  $.116M$ . The results of the product analysis and the following trial were: mole weight per ceric =  $397 \pm 1$ .

After recrystallization of the product from hot acetic acid-acetic anhydride and restandardization of the ferrous, the mole weight per ceric was obtained as 377, compared to an expected value (theoretical) of 376.

Solid state reflectance spectra of several known cerous and ceric compounds and of the product were taken from 250 millimicrons to 800 millimicrons on a Beckman Ratio Recording Reflectance Spectrophotometer. The ceric state in ceric ammonium sulfate had a peak at about 400 millimicrons, while the cerous state in cerous acetate and cerous carbonate had a peak at about 315 millimicrons. The product had a peak at about 400 millimicrons, and was almost identical in shape to the ceric ammonium sulfate spectrum.

The product was analyzed for acetate content via gas-liquid chromatography. Two solutions of propionic acid (distilled 138-139°) were prepared by weighing the acid into a 100 ml. volumetric flask and filling to the mark with water. The first solution contained 2.8944 gm. of acid per 100 ml. and the second contained 1.5489 gm. per 100 ml. (approx. .001M and .002M). At room temperature the error due to volume change in the flask and the liquids should have been of the order of a per cent or less. The sample to be analyzed was weighed into a 50 ml. flask. It was then suspended by swirling in trifluoroacetic acid (Matheson, Coleman and Bell, Norwood, Ohio). It was found that about .06 gm. of product in 6 gm. of trifluoroacetic acid gave the most complete solution. A few ml. of water were added with swirling, and complete solution was effected. A given volume (usually 5.0 ml.) of propionic acid solution was then added with a pipette, the sample was stirred, and an injection in the gas chromatograph was made. The column had previously been calibrated for peak ratio as a function of the mass ratio of propionic to acetic, so that a quantitative analysis of the acetate content was possible.

The column used was a 20% FFAP on acid washed Chrom W (60/80) two feet long by 1/8" in stainless steel. It was used on an Aerograph HyFi Model 600 gas chromatograph with a column temperature of about 130° and an injector temperature of 150°. To calibrate the column 1.1126 gm. of trifluoroacetic acid was weighed into a flask closed with a septum, and 5.0 ml. of the solution about .002M in propionic acid was added with a pipette, followed by .0738 gm. of acetic acid. The sample had a peak ratio of 3.44 and a mass ratio of 1.96. Additional acetic acid was repeatedly weighed into the system, followed by injections on the GC.

A given ratio of acetic and propionic acids was placed in a flask sealed with a septum and the peak ratio was determined with various amounts of trifluoroacetic acid added. Over a wide range of trifluoroacetic acid concentrations (from 0 to 8.4255 grams in a typical analysis volume) it was observed that the trifluoroacetic acid concentration had no apparent effect upon the ratio of the peaks of propionic and acetic acids.

A sample of the product was put in solution and injected periodically over a period of over 2 hours. The five injections that were made over a period of 45 minutes showed no change in the mass of acetic acid in the flask. When a final injection was made after two hours, however, the acetic acid analysis had dropped considerably. The mean of the first five trials was a mole weight per 4 acetates of  $359 \pm 7$ .

Magnetic moments<sup>7</sup> were determined for several known cerous and ceric compounds and for the product by the Gouy method using a Varian Associates V4404 electromagnet, a V2300A power supply, and a V2301A current regulator. All samples were dried 24 hours in vacuo at room temperature over KOH and calcium chloride. The results were corrected for the diamagnetism of the glass and of the ligands and were corrected for the air displaced. All data were taken twice with at least thirty minutes between repetitive measurements. All data were taken at each of 4 amperages and 3 pole positions, giving 12 data points for each compound. The standard used was  $\text{Hg}(\text{Co}(\text{SNC})_4)$ , which was prepared by the method given by Schlesinger.<sup>8</sup> The standard was carefully recrystallized several times and was washed with water and ethanol. The data were taken at  $22.0^\circ$  except for a few measurements which were taken at  $25.0^\circ$  with temperature correction.

The gram susceptibility of the standard mercury tetrathiocyanatocobaltate was taken as  $16.44 (\pm 0.08) \times 10^{-6}$  at  $20^\circ$ .<sup>9</sup> This value was used

directly without the small change for the change of the susceptibility with temperature according to the Curie-Weiss law.

The following results were obtained:

Lindsay ceric sulfate (Code 291): effective moment =  $.812 \pm .073$  BM  
(11 values mean)

G. F. Smith Co. ceric ammonium nitrate analyzed by Smith Co. as 100.00% : slightly diamagnetic if anything, but very close to neutral

Shepherd Co. cerous acetyl-acetate :  $3.19 \pm .15$  BM

### 3. Results

In summary, a bright yellow salt has been prepared by ozonating a solution of cerous acetate in acetic acid-acetic anhydride in the presence of small amounts of nitrate required to maintain the solution of cerous acetate in the mixture. The ceric titer per unit mass seemed to vary with the exact process of preparation and drying, but values obtained by standard ferrous-ceric titrations were within about  $\pm 8\%$  of the theoretical ceric acetate values for all batches. The reflectance spectrum from 250 to 800 millimicrons corresponded to the spectrum for ceric salts, and the magnetic susceptibility indicated that the compound contained a small amount of cerous but was primarily in the ceric state. Gas-liquid chromatography gave results in the two trials of formula weights per 4 acetates of  $359 \pm 7$  and  $361 \pm 9$ . The ceric-ferrous titration for those particular samples indicated a formula weight per ceric of 394, and it was suspected that perhaps some decarboxylation could have taken place in the process of getting the product into solution. It was noted that upon thermal decomposition at  $105^\circ$  the ceric titer dropped to a formula weight of 300 per ceric, which would have been almost the exact titer of a mixture of

1:1 of the thermal decomposition products found by Patnaik and Sahoo.<sup>5</sup> The product decomposed photolytically in the presence of sunlight, losing its color and evolving gas. Preliminary gas chromatography of the gases showed that the masses were methane and carbon dioxide. Further characterization of the ceric acetate is in progress.

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UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) <b>Case Institute of Technology Department of Chemistry Cleveland, Ohio 44106</b>		2a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>	
3. REPORT TITLE <b>PHOTO-INDUCED REDOX REACTIONS</b>		2b. GROUP	
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) <b>Scientific Interim</b>			
5. AUTHOR(S) (First name, middle initial, last name) <b>Jay K Kochi Tristram W Bethea III Nelson E Hay</b>			
6. REPORT DATE <b>February 1967</b>	7a. TOTAL NO. OF PAGES <b>63</b>	7b. NO. OF REFS <b>9</b>	
8a. CONTRACT OR GRANT NO. <b>AF-AFOSR-226-63</b>	9a. ORIGINATOR'S REPORT NUMBER(S)		
b. PROJECT NO. <b>9710-02 61445014</b>	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) <b>AFOSR 67-0396</b>		
c. <b>681303</b>			
d.			
10. DISTRIBUTION STATEMENT <b>Distribution of this document is unlimited.</b>			
11. SUPPLEMENTARY NOTES <b>TECH, OTHER</b>		12. SPONSORING MILITARY ACTIVITY <b>AF Office of Scientific Research (SRC) 1400 Wilson Blvd., Arlington, Va. 22209</b>	
13. ABSTRACT Despite the ease of formation of silver ion complexes of olefins, photolysis of a variety of these complexes in several solvents afforded no apparent photo-reaction but the cuprous chloride-1,5-cyclooctadiene complex structure of which has been determined has been shown to undergo photoreaction in ether solution at 2537Å to produce tricyclo (3.3.0.0) octane. In the decarboxylation of cyclohexane carboxylic acid, the same products were obtained in the thermal reaction and in all of the photolytic ones. The esters and alkylbenzenes show the most pronounced differences in the two methods of decarboxylation; the combined yields of these components in the thermal reaction are over twice those obtained by any photolytic method. The decarboxylation of 2,2-dimethylbutyric acid, a tertiary acid, showed a more obvious difference. In the thermal reaction no 2-methylbutane was produced; in the photolytic reactions, however, this product was found. In the photolysis of primary carboxylic acids, shorter wavelength irradiation, 2537Å, produces greater amounts of alkene and dimer than does the 3500Å reaction. The 2537Å reaction also gives products, e.g. butane from n-butyric acid and pentane from n-valeric acid, which may be pictured as originating from the coupling of a methyl radical and the radical produced from the decarboxylation of the acid. The decarboxylation of acids with thallium(III) acetate has been found to proceed only photolytically, for all practical purposes.			

DD FORM 1473

1 NOV 65

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14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	<p>Olefins Photolysis Silver complexes Copper(I) complexes Decarboxylation Thermal reaction 2, 2-dimethylbutyric acid Irradiation Radical Thallium(III)</p>						