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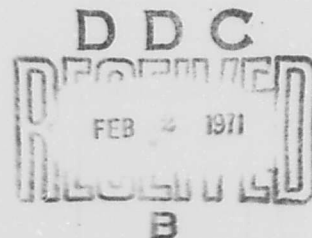
Final Report

Air Force Office of Scientific Research

AFOSR - 70-1874

Photo-Induced Redox Reactions

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Principal Investigator

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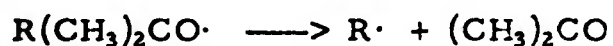
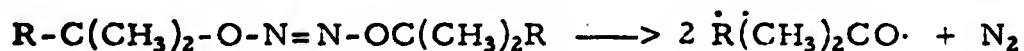
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This report represents the work which resulted from support from the Air Force of Scientific Research on Grant AFOSR ~~68-1347~~ 70-1874. The research covers three areas which are described as (1) the photolysis of heavy metal carboxylates, (2) the photolysis of acyl peroxides and (3) photochemical production of alkyl radicals and the reaction with metal oxidants.

The program has been directed towards the understanding of the redox reactions between organic free radicals and metal oxidants. Heavy metal carboxylates were successfully used to generate alkyl radicals by decarboxylation of the carboxylato ligand. Subsequent oxidation of the alkyl radicals by the metal oxidant was also studied in detail. Acyl peroxides were photolyzed in order to obtain an unambiguous source of alkyl radicals which we hope to apply in subsequent studies to metal oxidants.

Dialkyl hyponitrites generate alkyl radicals as follows:



Ethyl radicals generated in this manner reacted with cobalt(III) and copper(II) complexes. The results are given in Tables I and II.

Table I. The Oxidation of Ethyl Radicals by Copper(II) Complexes

Cu ^{II} Complex	C ₂ H ₄	C ₂ H ₆	(CH ₃) ₂ CO	Am ^t OH	Et L
None	0.02	1.42	1.35	0.14	-
(CH ₃) ₄ NBr	0.01	1.36	1.41	0.19	-
Cu ₂ (OAc) ₄	1.10		1.11	0.48	0
Cu(OAc) ₂ · 2H ₂ O	0.92		1.23	0.34	0.12
Cu(OAc) ₂ · 2H ₂ O · 2EtSCN	0	0	1.26	0.32	1.22 (EtSCN)
Cu(phen) ₂ Br ₂	0.01	0	1.27	0.33	1.22 (Et-Br)
Cu(tren)(SCN)(C ₂ N ₂ S)	0	0	1.22	0.34	1.08 (Et-NCS)

Table II. Oxidation of Ethyl Radicals by Cobalt(III) Complexes

Co ^{III} Complex	C ₂ H ₆	(CH ₃) ₂ CO	Am ^t OH	Et Br
None	1.42	1.35	0.14	-
(CH ₃) ₄ NBr	1.36	1.41	0.19	0
Co(NH ₃) ₅ Br ₃	0	1.11	0.37	1.11
Co(NH ₃) ₅ BrCl ₂	0	1.30	0.32	1.05 (Et-Cl)
Co(NH ₃) ₅ ClBr ₂	0	1.27	0.38	1.0
Co(NH ₃) ₅ Cl(ClO ₄) ₂	1.28	1.22	0.24	0
Co(NH ₃) ₅ Br(ClO ₄) ₂	1.20	1.24	0.14	0.09

Pair Production and Cage Reactions of Alkyl Radicals in Solution.

Roger A. Sheldon and Jay K. Kochi, J. Amer. Chem. Soc., 92, 4395 (1970).

Aliphatic diacyl peroxides undergo homolysis on ultraviolet irradiation at 30° to a pair of alkyl radicals and 2 mol of carbon dioxide. The quantum yield for carbon dioxide formation is 2 (2537 Å) and independent of the structure of the alkyl groups. The alkyl radicals are generated in sufficiently high steady state concentrations to enable the esr spectra of a variety of transient alkyl species to be recorded with excellent signal-to-noise ratios. The disproportionation and combination of alkyl-alkyl radical pairs formed in this manner are studied in various solvents and the results compared to those obtained in the gas phase. The cage processes of alkyl-alkyl radical pairs are delineated. The esr study of the rearrangement of cyclopropylmethyl and ω -hexenyl radicals indicates that the cage combination is fast and only those alkyl radicals which diffuse from the solvent cage are observed. In contrast to the thermolytic decomposition of diacyl peroxides, little or no esters are formed in the photolytic process.

Photolysis of Peresters. Reactions of Alkoxy-Alkyl Radical Pairs

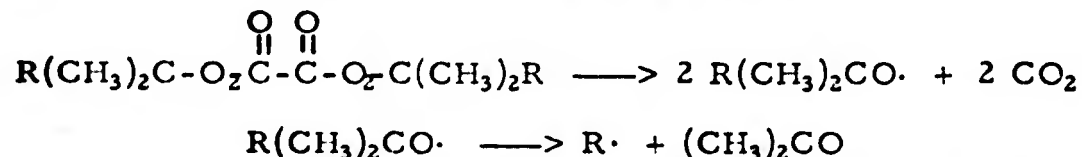
in Solution, Roger A. Sheldon and Jay K. Kochi, J. Amer. Chem. Soc., 92, 5175 (1970).

A series of peresters $\text{RCO}_2\text{OC}(\text{CH}_3)_2\text{R}'$ cleanly liberate 1 mol of carbon dioxide with a quantum yield of unity when irradiated in solution at 2537 Å. An alkyl radical $\text{R}\cdot$ and an alkoxy radical $\cdot\text{OC}(\text{CH}_3)_2\text{R}'$ are the first discernible intermediates. The electron spin resonance spectrum of the alkyl radical $\text{R}\cdot$ is obtainable when photolyses are carried out directly in the cavity of the spectrometer. The esr spectrum of $\text{R}'\cdot$ from the secondary fragmentation of the alkoxy radical is readily observed with isopropyl, t-butyl, and benzyl simultaneously with its partner $\text{R}\cdot$ at -115°, but is not seen when R' is methyl or ethyl. Reactions of the alkyl-alkoxy radical pair are considered to proceed from a solvent cage. Combination to form ether $\text{ROC}(\text{CH}_3)_2\text{R}'$ and disproportionation to alcohol $\text{R}'(\text{CH}_3)_2\text{COH}$ and alkene $\text{R}(-\text{H})$ are exclusively cage processes. The relative rates of disproportionation and combination k_d/k_c for alkyl-alkoxy and alkyl-alkyl radical pairs are compared and discussed in terms of the transition state for disproportionation. The yield of ether from t-butyl peracetate can be quantitatively related to the efficiency of the cage process in a series of solvents. Cage reactions in the thermal and photochemical decomposition of peresters are qualitatively compared. Examination of the rearrangement of cyclopropylmethyl radical leads to an estimate of 10^9 sec^{-1} for the combination of an alkyl and an alkoxy radical pair.

Thermal Decomposition of Some t-Alkyl Peroxyoxalates, Roger A.

Sheldon and Jay K. Kochi, J. Org. Chem., 35, 1223 (1970).

A variety of t-alkyl peroxy oxalates was synthesized and their thermal decomposition studied in various solvents.



The incursion of ionic routes to decomposition were observed in polar solvents.

Free Radicals in Thermal and Photochemical Oxidative Decarboxylations

with Lead(IV), Jay K. Kochi, John D. Bacha, and Tristram W. Bethea, III, J. Amer. Chem. Soc., 89, 6538 (1967).

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

Photochemical Decarboxylation of Acids with Thallium(III), Jay K. Kochi

and Tristram W. Bethea, III, J. Org. Chem., 33, 75 (1968).

Tl(III) carboxylates generated by the facile metathesis of Tl(III) acetate and a variety of carboxylic acids are photolyzed at 2537 and 3500 Å in benzene solutions. Photolysis yields Tl(I) carboxylate and CO₂ quantitatively together with products derived from the alkyl moiety of the acid. These are alkane, alkene, dialkyl and alkyl esters, and alkylbenzene. The relative amounts of each depend on the irradiating source. Alkyl dimers are formed in high yields with 2537-Å light, whereas at 3500-Å alkanes are the major products. These products are considered to arise from free alkyl radicals generated by photolytic homolysis of Tl(III) carboxylates stepwise to Tl(II) carboxylates, followed by further fragmentation to the Tl(I) product. The good yields of dimers particularly from primary acids using 2537-Å irradiation is attributed to high local concentrations of radicals due to the instability of the Tl(II) species generated in an excited state. These alkyl radicals can be trapped by hydrogen donors or scavenged by Cu(II). The rearrangement of 5-hexenyl radical from 6-heptenoic acid to cyclopentylmethyl radical is not reversible and direct molecular processes do not obtain in the dimerization.

Formation and Oxidation of Alkyl Radicals by Cobalt(III) Complexes,

Sheldon S. Lande and Jay K. Kochi, J. Amer. Chem. Soc., 90, 5196 (1968).

The homolysis of Co^{III} carboxylates, formed by metathesis of Co^{III} acetate in a carboxylic acid medium follows first-order kinetics. The products derived from the decarboxylation of the acid arise from an alkyl radical precursor. Primary and secondary propyl radicals from *n*-butyric and isobutyric acids, respectively, afford principally propane by hydrogen transfer from solvent. Oxidation by Co^{III} is a minor reaction. These radicals are, however, readily intercepted by catalytic amounts of Cu^{II} salts and propylene is generated in quantitative yields. On the other hand, *t*-butyl radicals from the decarboxylation of pivalic acid are readily oxidized by Co^{III} . *t*-Butyl radicals are trapped efficiently by oxygen, and the regeneration of Co^{III} from Co^{II} by reaction with *t*-butylperoxy and *t*-butoxy radicals allows for the catalytic oxidative decarboxylation of pivalic acid. Strong acids markedly enhance the rates of both decarboxylation and oxidation of alkyl radicals by Co^{III} . Cationic carboxylatocobalt(III) complexes, proposed as the reactive species responsible for facile homolysis, are also capable of the oxidation of primary and secondary alkyl radicals as well as alkenes. Carboxylate salts also promote decarboxylation by Co^{II} via anionic carboxylatocobaltate(III) complexes. The latter, however, are ineffective toward primary and secondary alkyl radicals. A mechanism for the oxidation of alkyl radicals by various Co^{III} complexes is proposed.

Photochemical and Thermal Reduction of Cerium(IV) Carboxylates. Formation

and Oxidation of Alkyl Radicals, Roger A. Sheldon and Jay K. Kochi,

J. Amer. Chem. Soc., 90, 6688 (1968). . .

The photochemical and thermal reduction of Ce^{IV} carboxylates to Ce^{III} proceed by decarboxylation and liberation of alkyl radicals. Alkanes are subsequently formed by hydrogen transfer, and alkenes, together with esters, result from oxidation of alkyl radicals by Ce^{IV} . *n*-Propyl and isopropyl radicals primarily afford propane, whereas *t*-butyl radicals are oxidized to isobutylene and *t*-butyl esters. The mechanism of the oxidation of alkyl radicals by Ce^{IV} is discussed. Quantum yield measurements show that photochemical homolysis of Ce^{IV} carboxylates is an efficient process. The thermal and photochemical reactions are otherwise equivalent. Alkyl radicals can be trapped with oxygen, chloroform, or Cu^{II} . If excess oxygen is employed a catalytic decarboxylation of pivalic acid occurs. Strong acids accelerate both the thermal and photochemical reduction of Ce^{IV} . Cationic carboxylatocerium(IV) species which are labile to homolysis and readily reduced by alkyl radicals are postulated as the reactive intermediates in the presence of acid.

Cerium(IV) Acetate, Nelson E. Hay and Jay K. Kochi, J. Inorg. Nucl. Chem.,

Vol. 30, pp. 884-886 (1968).

The preparation and characterization of cerium(IV) acetate is described.

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