Table IX. Analyses of Alkylcobalt Derivatives of Cobalt(salen), by Alkylation in Aqueous Medium

Alkyl group	Axial base	Formula	Calcd, % C	Calcd, % H	Calcd, % Co	Found, % C	Found, % H	Found, % Co
CH_3	H_2O	$C_{17}H_{19}N_2O_3Co$	57.11	5.62		57.05	5.66	
C_2H_5	H_2O	$C_{18}H_{21}N_2O_3Co$	58.07	5.69		58.21	5.70	
n-C_3H_7	H_2O	$C_{19}H_{23}N_2O_3Co$	59.07	6.00	15.25	58.83	5.91	14.87
i-C_3H_7	H_2O	$C_{19}H_{23}N_2O_3Co$	59.07	6.00	15.25	59.12	5.91	15.10
$CH_2C(CH_3)_3$	H_2O	$C_{21}H_{27}N_2O_3Co$	60.88	6.57	14.22	60.84	5.52	14.61
$CH{=}CH_2$	Py	$C_{23}H_{22}N_3O_2Co$	64.04	5.15	13.66	63.88	5.01	13.37
CH_2Cl	H_2O	$C_{17}H_{18}N_2O_3Co$	51.99	4.62	15.01	52.18	4.56	14.79

Photolysis Procedure. Solutions of the alkylcobalt complexes containing 10–20 mg of the crystalline solids in 1.5 ml of water or buffer solutions (Clark and Lubs) were prepared in test tubes which were sealed off with rubber serum caps. They were made anaerobic by first evacuating them with an oil pump and permitting the solution to boil. Subsequently the tubes were filled with argon (99.998% purity) to about 5 lb above atmospheric pressure. The photolysis light source was two 150-W GE projector spot lamps which were placed at a distance of 20 cm from the sample tubes. During the illumination a stream of cold air was blown over the tubes to prevent the temperature of the solutions rising above 35°. The time of irradiation was varied between minutes and days, depending on the compounds and their photolysis rate. In the case of methylcobalamin and methylcobaloxime a study of the time dependence of the methane–ethane production ratio on photolysis was undertaken, but no significant change was noted over a period of 24 hr of irradiation under these conditions. If the solubility of the samples was insufficient, suspensions of the finely powdered compounds were made. The sample tubes containing the suspensions were mechanically shaken during the photolysis.

Pyrolysis Experiments. Unless indicated otherwise, all samples were placed into test tubes, covered with serum caps, and made anaerobic as described above. The thermal decomposition was carried out by placing the sample tubes into a thermostatically controlled oil bath at temperatures between 215 and 225°.

Identification of Products. The photolysis and pyrolysis products were analyzed by gas chromatography utilizing a $^1/_8$ in. × 5 ft Poropak Q column at a helium flow rate of 25 cc/min, and a flame ionization detector. Excellent resolution was obtained by running isothermally (at 65°) for 2–5 min and then programming at a 15° temperature increase per minute to 170°. Under these conditions the following retention times were observed (in seconds): methane, 0; ethane, 70; propane, 280; *n*-butane, 495. The relative molar concentrations were obtained by comparing peak heights with a standard gas mixture. All results are given in relative mole per cent.

Joint Photolysis of Methylcobaloxime and Vitamin B_{12r}. Vitamin B_{12a} (10 mg, 5 ml of water) was treated with 15 mg of $NaBH_4$ under argon. Acetic acid (two drops) was added and the solution was allowed to stand until H_2 evolution ceased. Next there was added 10 mg of methyl(pyridine)cobaloxime. The solution was irradiated and shaken for 2 hr under argon. Paper chromatography of the reaction solution on tlc showed the presence of vitamin B_{12a} and methylcobalamin by comparison of the R_f values with authentic samples (solvent: butanol–2-propanol–water–acetic acid (100:100:100:3)).

Mass spectrographic analyses were performed at Shell Development Co., Emeryville, Calif., using a quadrupole mass spectrograph (EAI Quad 300). Prior to measurement the gases were absorbed on a Poropak column.

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

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Abstract: 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) salts have been widely employed as strong oxidants in aqueous solutions.[1] Cerimetry is a well-established analytical technique, since a variety of inorganic species as well as organic functional groups are readily oxidized.[2] The photochemical reduction of Ce^{IV} salts, particularly sulfate, perchlorate, and nitrate, in aqueous solutions has also

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[1] For a pertinent review, see W. Richardson, "Oxidations in Organic Chemistry," K. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter 4.

[2] G. Smith, "Cerate Oxidimetry," G. F. Smith Chemical Co., 1942.

been extensively studied.[3–7] Recently, transient radical species have been identified during flash photolytic decomposition of Ce^{IV} nitrate and sulfate in aqueous solutions.[8]

We are intrigued by the dual thermal and photochemical behavior of this versatile reagent. In particular, the capacity of Ce^{IV} as a 1-equiv oxidant, and the role of free radicals as intermediates during oxidation of organic compounds, require elaboration.

The Ce^{IV}-induced decarboxylation of aliphatic acids provides an ideal system for examining these questions. For example, the standard (half-cell) reaction for decarboxylation is given by eq 1. The formation of alkyl

$$RCO_2^- \longrightarrow R\cdot + CO_2 + e \qquad (1)$$

radicals (R·) is diagnostic of a 1-equiv oxidation. Furthermore, the subsequent oxidation of alkyl radicals by Ce^{IV} must also compete with other facile reactions of alkyl radicals (such as hydrogen transfer). This competition has been successfully used in studies of oxidation of alkyl radicals by a variety of metal oxidants.[9, 10]

Oxidation of oxalic and malonic acids by Ce^{IV} was one of the early developments in cerimetry.[11, 12] Although α-hydroxy acids are readily oxidized,[13] simple aliphatic acids are resistant to Ce^{IV} sulfate in refluxing aqueous solutions of dilute sulfuric acid.[12]

Nonaqueous solutions offer a number of advantages for the promotion and study of oxidation reactions.[14] Solutions of Ce^{IV} salts in glacial acetic acid are photochemically unstable,[6] and the thermal decomposition is enhanced by perchloric acid.[15] We examined the decarboxylation of three representative acids: *n*-butyric, isobutyric, and pivalic acids, by Ce^{IV} acetate in the carboxylic acid as solvent, and we hope to demonstrate the primacy of free alkyl radicals as intermediates. The mechanism of the decarboxylation of acids and the subsequent oxidation of alkyl radicals by Ce^{IV} is the principal objective of this study.

Results

Cerium(IV) Acetate in Carboxylic Acid Media. Solutions of Ce^{IV} acetate[16] in a variety of carboxylic acids are yellow-orange. The electronic absorption spectra of Ce^{III} and Ce^{IV} acetates in *n*-butyric acid are shown in Figure 1. Metathesis among Ce^{IV} carboxylates (eq 2) is rapidly established, and the appropriate Ce^{IV} carboxylate can be readily prepared by removal of acetic acid.

$$Ce^{IV}(OAc)_4 + 4RCO_2H \rightleftarrows Ce^{IV}(O_2CR)_4 + 4HOAc \qquad (2)$$

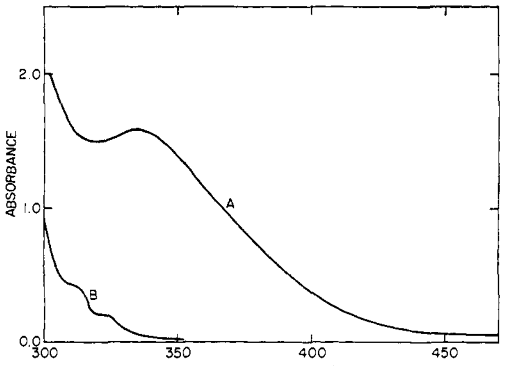

Figure 1. Absorption spectra of $Ce^{IV}(OAc)_4$ (curve A, 5.05×10^{-4} *M*) and $Ce^{III}(OAc)_3$ (curve B, 3.90×10^{-4} *M*) in *n*-butyric acid.

A solution of 0.1 *M* Ce^{IV} isobutyrate in isobutyric acid afforded the same yields of products as a solution of Ce^{IV} acetate under equivalent conditions. Similarly, Ce^{IV} pivalate was practically indistinguishable from Ce^{IV} acetate in pivalic acid solutions. For convenience, we chose to examine the thermolysis and photolysis of Ce^{IV} carboxylates by preparing dilute (0.1 *M*) solutions of Ce^{IV} acetate in the chosen acid as solvent.

Photochemical Reduction of Ce^{IV} Carboxylates. The photolysis of Ce^{IV} carboxylates was examined mainly at 3500 Å, and comparative studies were also done at 2537 Å (Table I). The former was preferred since the absorption spectrum of the photolyzed solution indicated reduction to Ce^{III} carboxylate, and the latter does not absorb appreciably above 3300 Å (Figure 1). Photolyses were carried out at 30° in quartz tubes from which oxygen was removed by flushing the solution with a stream of helium. The reduction of Ce^{IV} was readily followed visually. Ce^{III} carboxylates were stable to irradiation at 3500 Å, and underwent no perceptible change at 2537 Å under our experimental conditions. Deliberate addition of Ce^{III} had no effect on the products derived from the photolysis of Ce^{IV} at either 3500 or 2537 Å.

Acetic Acid. Carbon dioxide and methane were the major products from the 3500-Å irradiation of a solution of Ce^{IV} acetate in glacial acetic acid (eq 3).[17] A

$$Ce^{IV}(O_2CCH_3)_4 \longrightarrow Ce^{III}(O_2CCH_3)_3 + CH_4 + CO_2 \qquad (3)$$

small amount of methyl acetate, ethane, and acetoxyacetic and succinic acids were also found. The latter acids were not preferentially decarboxylated, since deliberate addition caused no change in products (particularly methyl acetate), and 80% of the acids could be accounted for as the methyl esters after treatment with diazomethane.

***n*-Butyric Acid.** The photolysis of Ce^{IV} in *n*-butyric acid at 2537 and 3500-Å yielded principally carbon dioxide and propane. Propylene was formed in 2% yield, and only traces of propyl esters were detected.

$$Ce^{IV}(O_2CCH_2CH_2CH_3)_4 \longrightarrow Ce^{III}(O_2CCH_2CH_2CH_3)_3 + CH_3CH_2CH_3 + CO_2 \qquad (4)^{17}$$

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(17) The reaction is not stoichiometric (see Discussion), and the equation is not balanced.

Table I. Photochemical Decarboxylation of Acids by Ce$^{\text{IV}}$ Acetate[a]

Acid R-CO$_2$H	Irradiation, Å	Additive (M)	Time of irradiation, min	Products, mol %: CO$_2$[b]	RH[c]	R(-H)[c]	Ester[c]	ΣR/CO$_2$
CH$_3$	3500	None	240	65	77		3[f]	
CH$_3$CH$_2$CH$_2$	3500	None	240	89	98	2	*d*	1.0
CH$_3$CH$_2$CH$_2$	2537	None	240	87	79	2	*d*	0.81
CH$_3$CH$_2$CH$_2$	2537	Ce(OAc)$_3$ (0.050)	240	90	79	2	*d*	0.81
CH$_3$CH$_2$CH$_2$	3500	LiOAc (0.20)	180	97	88	2		0.90
CH$_3$CH$_2$CH$_2$	3500	LiO$_2$CCF$_3$ (0.20)	180	96	84	2		0.86
(CH$_3$)$_2$CH	3500	None	120	65	64	14	4[g]	0.82
(CH$_3$)$_3$C	3500	None	80	49	*e*	72	8[h]	0.80

[a] In 5-ml solutions of 0.10 M Ce$^{\text{IV}}$(OAc)$_4$ in carboxylic acid at 30°. [b] Based on 1Ce$^{\text{IV}}$ → 1CO$_2$. [c] Expressed as per cent of CO$_2$ yield. [d] Approximately 0.1% *n*-propyl butyrate and isopropyl acetate and butyrate. [e] Approximately 0.1% isobutane. [f] Methyl acetate. [g] 1% isopropyl acetate and 3% isopropyl isobutyrate. [h] 4% *t*-butyl acetate and 4% *t*-butyl pivalate.

Table II. Effect of Strong Acids on the Photochemical Decarboxylation of Acids by Ce$^{\text{IV}}$ Acetate[a]

Acid R-CO$_2$H	Additive (M)	Time of irradiation, min	Product, mol %: CO$_2$[b]	RH[c]	R(-H)[c]	Ester[c]	ΣR/CO$_2$
CH$_3$	HClO$_4$ (0.6)	70	43	75		19[d]	0.94
CH$_3$CH$_2$CH$_2$	HClO$_4$ (0.05)	240	94	66	2	*e*	0.68
CH$_3$CH$_2$CH$_2$	HClO$_4$ (0.15)	120	51	20	18	22[f]	0.60
CH$_3$CH$_2$CH$_2$	HClO$_4$ (0.3)	30	43	7	26	42[g]	0.75
CH$_3$CH$_2$CH$_2$	HClO$_4$ (0.6)	15	44	3	27	64[h]	0.94
CH$_3$CH$_2$CH$_2$	CF$_3$CO$_2$H (2)	240	73	23	1	3[i]	0.27
CH$_3$CH$_2$CH$_2$	BF$_3$ (0.2)	80	80	64	2		0.66
CH$_3$CH$_2$CH$_2$	C$_5$H$_5$N (2)	240	53	22	3	*e*	0.25
(CH$_3$)$_2$CH	HClO$_4$ (0.6)	10	51	4	27	31[j]	0.62
(CH$_3$)$_2$CH	HClO$_4$[m] (0.6)	10	36	1	33	40[k]	0.74
(CH$_3$)$_3$C	HClO$_4$ (0.6)	2	47	<0.1	<0.1	40[l]	0.40

[a] Solutions (5 ml) of 0.1 M Ce$^{\text{IV}}$(OAc)$_4$ in carboxylic acid irradiated at 3500 Å and 30°. [b] Based[4] on 1Ce$^{\text{IV}}$ → 1CO$_2$. [c] Expressed as per cent of CO$_2$ yield. [d] Methyl acetate. [e] <0.1% *n*-propyl butyrate, isopropyl acetate, and butyrate. [f] 8% *n*-propyl butyrate and 14% isopropyl butyrate. [g] 9% *n*-propyl acetate and 33% isopropyl butyrate. [h] 14% *n*-propyl butyrate and 50% isopropyl butyrate. [i] 3% *n*-propyl butyrate and <0.1% isopropyl acetate and butyrate. [j] 2% isopropyl acetate and 29% isopropyl isobutyrate. [k] 1% isopropyl acetate and 39% isopropyl isobutyrate. [l] *t*-Butyl acetate and pivalate. [m] Isobutylene (0.4 mmol) added.

Addition of pyridine, lithium acetate, or trifluoroacetate caused only minor effects (Table I).

Isobutyric Acid. Although propane was still the major product, the decarboxylation of isobutyric acid by Ce$^{\text{IV}}$ afforded significantly larger amounts of propylene and propyl esters compared to *n*-butyric acid, as shown in Table I.

$$\mathrm{Ce^{IV}[O_2CCH(CH_3)_2]_4 \longrightarrow Ce^{III}[O_2CCH(CH_3)_2]_3 + CH_3CH_2CH_3 + CO_2} \quad (5)^{17}$$

Pivalic Acid. Decarboxylation of pivalic acid by Ce$^{\text{IV}}$ at 3500 Å gave principally isobutylene, together with small amounts of *t*-butyl esters (Table I). Isobutane was formed only in trace amounts.

$$\mathrm{2Ce^{IV}[O_2CC(CH_3)_3]_4 \longrightarrow 2Ce^{III}[O_2CC(CH_3)_3]_3 + (CH_3)_2C{=}CH_2 + (CH_3)_3CCO_2H + CO_2} \quad (6)$$

Quantum Yields. The quantum yield for the formation of carbon dioxide varied with the acid and the concentration of Ce$^{\text{IV}}$. In 0.1 M Ce$^{\text{IV}}$ solutions at 3600 Å, the quantum yield decreased from 1.11 ± 0.07 for pivalic acid to 0.81 ± 0.05 for isobutyric acid and 0.52 ± 0.05 for *n*-butyric acid (average of five determinations each). In 0.010 M solutions of Ce$^{\text{IV}}$ in pivalic acid, the value of $\phi^{\mathrm{CO_2}}$ was 0.95 ± 0.06 (average of five determinations). These measurements were obtained on reductions which were carried to only 2-3% conversion. A small correction was made for a slow dark reaction.

Effect of Acids on the Photoreduction of Ce$^{\text{IV}}$. When perchloric acid was added to a solution of Ce$^{\text{IV}}$ in *n*-butyric acid, the rate of the photochemical reduction (3500 Å) increased dramatically (Table II). The decarboxylation of acetic, isobutyric, and pivalic acids was similarly affected by perchloric acid. No reaction occurred in the absence of Ce$^{\text{IV}}$.

The effect of perchloric acid on the product distribution was even more striking. Increase in perchloric acid resulted in diminution in alkane and concomitant increase in alkene and ester. The stoichiometry of the decarboxylation approached eq 7 at high acid concentrations.

$$\mathrm{2(PrCO_2)_4Ce^{IV} \xrightarrow[PrCO_2H]{H^+} 2(PrCO_2)_3Ce^{III} + [CH_3CH{=}CH_2 + PrO_2CPr] + H^+ + CO_2} \quad (7)$$

However, further thermal reactions of alkenes catalyzed by perchloric acid caused a lowering of the material balance (*vide infra*). The products from acetic acid were affected less by perchloric acid than the others. Methane was the principal product even at high concentrations, although there was a significant increase in methyl acetate (Table II).

Boron trifluoride and trifluoroacetic acid also induced the photochemical decarboxylation of Ce$^{\text{IV}}$. Compared to perchloric acid, however, the products were not as effectively diverted to alkenes and esters by these acids.

Table III. Effect of Radical Traps on the Photochemical Decarboxylation of Acids by Ce^{IV} Acetate[a]

Acid R–CO_2H	Additive (M)	Irradiation time, min	Products, mol %					$\Sigma R/CO_2$
			CO_2[b]	RH[c]	R(–H)[c]	Ester[c]	Others[c]	
CH_3	O_2[d]	300	85	25		7[h]	66[i]	0.98
CH_3	$HClO_4$ (0.6), O_2[e]	70	36	10		84[h]		0.94
$CH_3CH_2CH_2$	$HClO_4$ (0.3), $CHCl_3$ (6)	45	32	75	1			0.76
$CH_3CH_2CH_2$	$HClO_4$ (0.6), O_2[e]	45	39	2	1			0.03
$CH_3CH_2CH_2$	$Cu^{II}(OAc)_2$ (0.005)	240	56	3	88			0.91
$(CH_3)_2CH$	$HClO_4$ (0.6), $CHCl_3$ (6)	5	23	4	18	*l*		0.22
$(CH_3)_2CH$	$HClO_4$ (0.6), O_2[e]	10	66	<0.1	8	14[j]		0.22
$(CH_3)_3C$	O_2[d]	100	65	<0.1	33	<0.1	70[k,p]	1.0
$(CH_3)_3C$	O_2[f]	840	450	*l*	*l*	*l*	474[m,p]	1.0
$(CH_3)_3C$	O_2[g]	2880	*l*	*l*	*l*	*l*	2280[n,p]	
$(CH_3)_3C$	$HClO_4$ (0.6), O_2[e]	10	58	<0.1	<0.1	<0.1	20[o]	
$(CH_3)_3C$	$CHCl_3$ (6)	60	52	16	31	*l*	*l*	

[a] Solutions (5 ml) of 0.1 M $Ce^{IV}(OAc)_4$ irradiated at 3500 Å and 30°. [b] Based on $1Ce^{IV} \rightarrow 1CO_2$. [c] Expressed as per cent of CO_2 yield. [d] Solution flushed with O_2 before photolysis. [e] Solution flushed with oxygen before addition of $HClO_4$, then photolyzed. [f] Oxygen bomb experiment. [g] Oxygen bubbled through solution during photolysis. [h] Methyl acetate. [i] Methanol. [j] 1% isopropyl acetate and 13% isopropyl isobutyrate. [k] 37% *t*-butyl alcohol, 16% di-*t*-butyl peroxide, and 17% acetone. [l] Not determined. [m] 400% alcohol, 40% peroxide, and 34% acetone. [n] 1660% alcohol, 360% peroxide, and 260% acetone. [o] Acetone. [p] Yields based on Ce^{IV}.

Table IV. Competitive Decarboxylation of (A) Pivalic Acid and (B) *n*-Butyric or Isobutyric Acid by Ce^{IV} Acetate[a]

A/B[b] mol/mol	Products, mol × 10^4 [c]					$(C_3H_7)_{ox}$[d]/ (C_3H_8)	$(C_4H_9)_{ox}$[e]/ i-C_4H_{10}	$(\Sigma C_4H_9/\Sigma C_3H_7)(B$[f]$/A)$
	CO_2	C_3H_8	C_3H_6	i-C_4H_{10}	i-C_4H_8			
			B = Isobutyric Acid					
B	3.25	2.10	0.43			0.23		
0.090	2.96	1.74	0.38	0.020	0.19	0.24	10	1.1
0.20	2.75	1.22	0.31	0.030	0.37	0.28	13	1.4
0.55	2.67	0.94	0.29	0.040	0.70	0.34	19	1.2
1.2	2.58	0.52	0.25	0.045	1.1	0.54	25	1.4
1.2[g]	2.60	0.0	1.00	0.0	1.22			1.0
3.3	2.45	0.18	0.18	0.028	1.3	1.1	50	1.2
5.0	2.40	0.098	0.16	0.020	1.4	1.8	75	1.2
7.4	2.40	0.062	0.14	0.015	1.5	2.6	110	1.1
A	2.40			0.012	1.7		160	
			B = *n*-Butyric Acid					
B	4.15	3.65	0.080			0.023		
0.090	3.65	2.85	0.11	0.002	0.17	0.042	95	0.7
0.20	3.05	2.41	0.12	0.0025	0.23	0.051	100	0.5
0.55	2.65	1.00	0.11	0.0065	0.60	0.097	99	1.1
1.2	2.50	0.45	0.13	0.010	0.98	0.31	104	1.6
1.2[g]	2.60	0.0	1.10	0.0	1.17			0.9
3.3	2.45	0.18	0.11	0.012	1.38	0.66	121	1.5
5.0	2.37	0.090	0.089	0.012	1.46	1.04	130	1.7
7.4	2.40	0.040	0.068	0.012	1.52	1.77	148	1.9
A	2.40			0.012	1.70		160	

[a] In 0.1 M solutions of $Ce^{IV}(OAc)_4$ in carboxylic acid mixture, irradiated at 3500 Å and 30°. $Ce^{IV}(OAc)_4 = 5.0 \times 10^{-4}$ mol. [b] A = pivalic acid, B = *n*-butyric or isobutyric acid. [c] Only propane, propylene, isobutane, and isobutylene analyzed. [d] $(C_3H_7)_{ox}$ includes propylene and propyl esters obtained by extrapolation. [e] $(C_4H_9)_{ox}$ includes isobutylene and *t*-butyl esters by extrapolation. [f] ΣC_4H_9 and ΣC_3H_7 includes all products derived from *t*-butyl and propyl radicals, respectively. [g] $Cu^{II}(OAc)_2$ (5 mol %) added.

The Effect of Radical Scavengers on Products. Oxygen effectively reduced alkane yields during the photochemical reduction of Ce^{IV} in acetic, *n*-butyric, isobutyric, and pivalic acids under a variety of conditions listed in Table III. Methanol was the principal product from acetic acid (formaldehyde and formic acid were not analyzed). Photolysis in the presence of perchloric acid afforded methyl acetate, which undoubtedly arose from esterification of methanol subsequent to formation. The diminished amounts of methane were not truly indicative of the effectiveness of oxygen scavenging, since no effort was made to maintain oxygen in solution during photolysis.

Pivalic acid could be catalytically decarboxylated by Ce^{IV} in the presence of oxygen. If the reaction vessel was simply flushed with oxygen, and then photolyzed, the yield of isobutylene diminished and *t*-butyl alcohol, di-*t*-butyl peroxide, and acetone were found in significant quantities. The reaction sealed under 40-psig oxygen pressure led to more than a stoichiometric amount of *t*-butyl alcohol. Furthermore, bubbling oxygen through the reaction mixture during photolysis led to overwhelming amounts of *t*-butyl alcohol, di-*t*-butyl peroxide, and acetone (Table III). Successively longer times were required for the reduction of Ce^{IV}. A solution of Ce^{III} in pivalic acid in the presence of excess di-*t*-butyl peroxide was unaffected by irradiation at 3500 Å.

Products from the photochemical decarboxylation of *n*-butyric and isobutyric acids by Ce^{IV} in the presence of oxygen were difficult to identify. We noted that the usual products, propane, propylene, and propyl

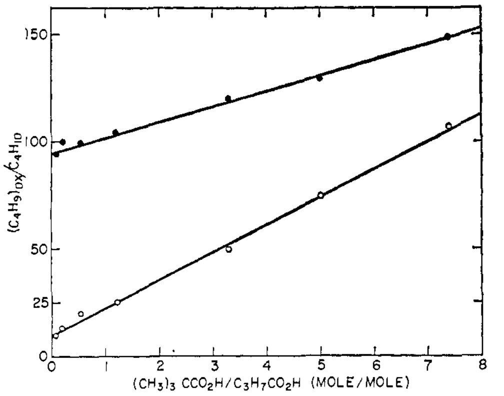

Figure 2. Oxidation/hydrogen transfer for *t*-butyl radicals from decomposition of Ce^{IV} in pivalic–*n*-butyric (●) and pivalic–isobutyric acid (○) mixtures.

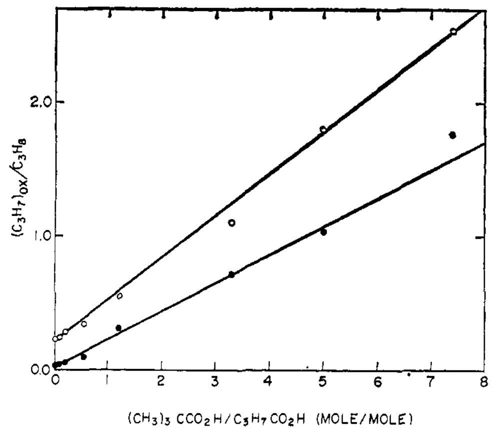

Figure 3. Oxidation/hydrogen transfer for *n*-propyl (●) and isopropyl radicals (○) from decomposition of Ce^{IV} in pivalic–*n*-butyric and pivalic–isobutyric acid mixtures, respectively.

esters, were absent and presumed that the *n*-propyl and isopropyl moieties were autoxidized.

Cupric acetate was also highly effective in diverting the course of decarboxylation of *n*-butyric acid by Ce^{IV}. At low concentrations, Cu^{II} does not absorb appreciably at 3500 Å, and was not involved in the primary photochemical process. Propane was completely quenched under these conditions.

Chloroform was partially effective in increasing isobutane yields from the photochemical decarboxylation of pivalic acid by Ce^{IV}. However, significant amounts of isobutylene still persisted. The *n*-propyl moiety from the perchloric acid induced decarboxylation of *n*-butyric acid (Table II) was completely converted by chloroform to propane.

Competitive Photochemical Decarboxylation of Acids by Ce^{IV}. Mixtures of pivalic acid and *n*-butyric or isobutyric acid were photochemically decarboxylated by Ce^{IV}. To simplify analysis only carbon dioxide, alkane (propane, isobutane), and alkene (propylene, isobutylene) were measured quantitatively. The yields of the accompanying esters were obtained by simple extrapolation of the data in Table I. The essential validity of this assumption was checked with competition studies in the presence of Cu^{II}. Alkenes were shown earlier to be the only significant products of decarboxylation in the presence of Cu^{II}. The consistency of these two sets of studies is given in the last column of Table IV.

From these competition studies it was possible to obtain the relative rates of over-all decarboxylation of pivalic, isobutyric, and *n*-butyric acids. Moreover, we could also determine the amounts of alkene (and ester) produced relative to alkane when *n*-propyl, isopropyl, and *t*-butyl radicals were generated under equivalent conditions. In these systems either *n*-butyric or isobutyric rather than pivalic acid was the principal hydrogen donor. The ratio of oxidation products (R_{ox} = alkene + ester) to alkane (RH) was linearly related to the composition of the carboxylic mixture (Figures 2 and 3).

Thermal Reduction of Ce^{IV} Carboxylates. Solutions of Ce^{IV} in carboxylic media were stable for days at room temperature when kept dark and anhydrous. If these solutions were freed of air and heated at 80° they underwent partial decarboxylation. Ce^{IV} was only incompletely reduced to Ce^{III} after 12 hr (Table V). Further heating caused no substantial change in the Ce^{IV} titer.

Table V. Thermal Decarboxylation of Acids by Ce^{IV} Acetate[a]

Acid $R\text{-}CO_2H$	Additive (*M*)	Products, mol % CO_2[b]	RH[c]	R(-H)[c]
CH_3	None	9	30	
$CH_3CH_2CH_2$	None	12	30	20
$CH_3CH_2CH_2$	LiOAc (0.2)	10	40	40
$CH_3CH_2CH_2$	LiO_2CCF_3 (0.2)	10	40	40
$CH_3CH_2CH_2$	NaOAc (0.2)	11	40	30
$(CH_3)_2CH$	None	14	10	30
$(CH_3)_3C$	None	15	10	40

[a] In solutions (5 ml) of 0.10 *M* $Ce^{IV}(OAc)_4$ heated *in vacuo* at 80° for 12 hr. [b] Based on $1Ce^{IV} \rightarrow 1CO_2$. [c] Expressed as per cent of CO_2 yield, estimated to nearest 10% due to small quantities. Esters not examined. Ce^{IV} not completely reduced.

Ceric acetate solutions in glacial acetic acid were reported to be thermally unstable in the presence of sodium acetate.[18] However, these solutions contained Pb^{IV} and Pb^{II}, which may have contributed to the thermal instability of Ce^{IV}. Sodium acetate, lithium acetate, or lithium trifluoroacetate had no noticeable effect on the decarboxylation of *n*-butyric acid by Ce^{IV}. Low yields of decarboxylation products still obtained (Table V).

The rate of the thermal decarboxylation of acids by Ce^{IV} was greatly enhanced by added mineral or Lewis acids. The perchloric acid induced decarboxylation values of acetic, *n*-butyric, isobutyric, and pivalic acids are given in Table VI. The decarboxylation of pivalic acid proceeded rapidly at room temperature under these conditions. We observed no reaction in the absence of Ce^{IV}.

In addition to promoting the decarboxylation, strong acids also had a marked effect on the products. Except for acetic acid, alkanes were minor and alkenes together with esters were major products. Esters were also partly formed by the acid-catalyzed addition of the carboxylic solvent to alkene. Thus propylene was converted in *n*-butyric acid to isopropyl butyrate by perchloric acid. However, a significant fraction of ester must have arisen by the direct oxidation of *n*-

(18) D. Benson and L. Sutcliffe, *Trans. Faraday Soc.*, **56**, 246 (1960).

Table VI. Thermal Decarboxylation of Acids by Ce^{IV} Acetate in the Presence of Acids[a]

Acid R-CO_2H	Additive (*M*)	Temp, °C	Reaction time,[b] min	Products, mol %				
				CO_2[c]	RH[d]	R(-H)[d]	Ester[d]	$\Sigma R/CO_2$
CH_3	$HClO_4$ (0.6)	80	2	39	68		15[e]	0.83
$CH_3CH_2CH_2$	$HClO_4$ (0.6)	80	1	42	3	28	52[f]	0.83
$CH_3CH_2CH_2$	BF_3	81	4	43	1	22	56[g]	0.78
$(CH_3)_2CH$	$HClO_4$ (0.6)	80	1	45	0.5	31	40[h]	0.72
$(CH_3)_2CH$	BF_3	81	6	46	1	42	50[i]	0.92
$(CH_3)_3C$	$HClO_4$ (0.6)	20	10	47	<0.1	<0.1	41[j]	0.41

[a] In 5-ml solutions of 0.1 *M* $Ce^{IV}(OAc)_4$ in carboxylic acid. [b] Time required for solution to become colorless. [c] Based on $1Ce^{IV} \rightarrow 1CO_2$. [d] Expressed as per cent of CO_2 yield. [e] Methyl acetate. [f] 14% propyl butyrate and 38% isopropyl butyrate, trace of isopropyl acetate. [g] 16% *n*-propyl butyrate, 38% isopropyl butyrate, and 2% isopropyl acetate. [h] Isopropyl isobutyrate and <0.1% isopropyl acetate. [i] 4% isopropyl acetate and 46% isopropyl isobutyrate. [j] 26% *t*-butyl acetate and 15% *t*-butyl pivalate.

propyl radicals since *n*-propyl butyrate was a relevant product in perchloric acid. No doubt some of this ester was isomerized by the strong acid, and the yields of *n*-propyl butyrate reported in Table VI must represent lower limits for direct oxidation.

Further reactions of alkene formed during decarboxylation in the presence of perchloric acid were more serious with isobutylene than with propylene. The product material balance from the decarboxylation of pivalic acid by Ce^{IV} (induced by perchloric acid) was poor (Table VI). We could show that even *t*-butyl alcohol, acetate, or pivalate were not stable under these conditions. The major products were 2,4,4-trimethylpentene-1 and -2.[19] Optimum results were obtained if the reaction was quenched immediately with sodium acetate and analyzed without delay.

Susceptibility of the products to further reactions in the presence of perchloric acid is related to the stability of the carbonium ion intermediate ($t\text{-Bu}^+ > i\text{-Pr}^+$, etc.). However, there is also an *oxidative* pathway for destruction of alkene by Ce^{IV} which increases in importance with acid strength.[20-23]

Alkyl radicals are also intermediates in the acid-catalyzed decarboxylation by Ce^{IV}. A solution of Ce^{IV} in pivalic acid was flushed with oxygen prior to the addition of perchloric acid. After a few minutes at room temperature this reaction yielded traces of hydrocarbon, only 12% *t*-butyl esters, together with di-*t*-butyl peroxide, *t*-butyl alcohol, and acetone. Meaningful analyses were obviated by the high acid concentrations (*vide supra*).

The autoxidative decarboxylation of pivalic acid was catalyzed by cerium carboxylates at elevated temperatures in the absence of acids. Either air or di-*t*-butyl peroxide (in the absence of air) oxidized Ce^{III} to Ce^{IV} at 100° in pivalic acid solutions. Subsequent reduction of Ce^{IV} by pivalic acid allows a catalytic decarboxylation to occur.

Discussion

The decomposition of Ce^{IV} carboxylates can be induced either photochemically or thermally. Reduction of Ce^{IV} to Ce^{III} accompanies the rate-determining homolysis and the liberation of alkyl radicals is simultaneous with decarboxylation. Alkyl radicals are accounted for as alkanes, alkenes, and esters and reasonable material balances with carbon dioxide are usually found.

The behavior of alkyl radicals from Ce^{IV} carboxylates does not depend on their mode of formation, and can be treated independently. In the following discussion, we will consider the decomposition of Ce^{IV} carboxylates, the role of alkyl radicals, and the oxidation of alkyl radicals by Ce^{IV} within this mechanistic framework.

Ce^{IV} Carboxylates. Ce^{IV} in aqueous solutions forms a variety of complexes, some mononuclear, others binuclear and polynuclear even in dilute solutions.[24,25] We avoided most of these ambiguities by employing Ce^{IV} carboxylate directly in carboxylic acid as solvent. These solutions follow Beer's law at 360 mμ down to less than 10^{-3} *M* Ce^{IV}. Deviations are observed at lower Ce^{IV} concentrations (Figure 4).

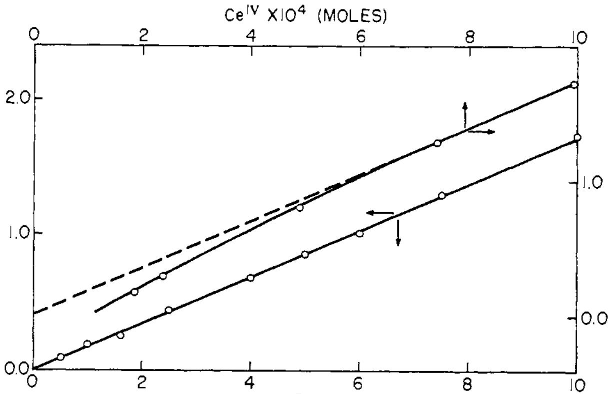

Figure 4. Dilution of $Ce^{IV}(OAc)_4$ in *n*-butyric acid monitored at 360 mμ: lower curve in 1-mm cell; upper curve in 1-cm cell.

Ce^{IV} trimers have been reported as the prevailing species in aqueous acetic acid solutions.[26] Ce^{IV} toluate is also extensively associated in benzene solutions[27] like the related Ce^{IV} alkoxides.[28] Pending more detailed studies, we shall treat Ce^{IV} carboxylates in carboxylic acid media as mononuclear species with the reservation in mind that higher orders are possible.[29]

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[19] From the acid-catalyzed dimerization of isobutylene.

[20] Similar oxidations of alkenes has been observed with Co^{III},[10,21] Pb^{IV},[22] and Tl^{III}.[23]

[21] C. Bawn and J. Sharp, *J. Chem. Soc.*, 1854, 1866 (1957).

[22] R. Norman and C. Thomas, *ibid.*, *B*, 776 (1967).

[23] J. Kochi and T. Bethea, *J. Org. Chem.*, **33**, 75 (1968), for some references.

[24] (a) M. Sherrill, C. King, and R. Spooner, *J. Am. Chem. Soc.*, **65**, 170 (1943); (b) L. Heidt and M. Smith, *ibid.*, **70**, 2476 (1948).

[25] T. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

[26] K. Wiberg and P. Ford, *Inorg. Chem.*, **7**, 369 (1968).

[27] H. Baker, J. O'Rear, P. Sniegoski, and R. Kagarise, *U. S. Naval Res. Lab. Rept.*, 5641 (1961).

[28] D. Bradley, A. Chatterjee, and W. Wardlow, *J. Chem. Soc.*, 2260 (1956); 2600 (1957).

Stoichiometry of the Decomposition of Ce^{IV} Carboxylates. The stoichiometry of the decarboxylation depends largely on the fate of the alkyl radical. If alkyl radicals are oxidized by Ce^{IV} subsequent to formation, then each mole of carbon dioxide results from 2 mol of Ce^{IV}. On the other hand, if radicals undergo hydrogen transfer and suffer bimolecular interactions, then Ce^{III} and carbon dioxide would be formed in equimolar quantities. The data in Tables I–VI should be examined with these values in mind.[30,31]

The material balance in the photochemical reduction of Ce^{IV} carboxylates given in Table I is fairly good. Most of the alkyl radicals can be accounted for as alkane, alkene, or alkyl ester (last column, Table I). The Ce^{IV}/CO_2 stoichiometry (1:1) given by eq 4 is applicable to *n*-butyric acid (column 5), since propane is the major product. On the other hand, the decarboxylation of pivalic acid by Ce^{IV} affords isobutylene and the 2:1 stoichiometry given by eq 6 is approximated. Isobutyric acid occupies an intermediate position.

Addition of perchloric acid to the photochemical decarboxylation of Ce^{IV} carboxylates causes a decrease in alkane yields and a concomitant increase in alkene and ester. The Ce^{IV}/CO_2 stoichiometry approaches 2:1 even with *n*-butyric acid (Table II).

The thermal decomposition of Ce^{IV} carboxylates and that induced by strong acid obey essentially the same stoichiometric relations as those given for the photochemical reductions. In the presence of strong acid, alkenes undergo further oxidation[20] with Ce^{IV}, and yields of carbon dioxide are diminished.

Decarboxylation of Acids by Ce^{IV}. We associate the decarboxylation of acids with the decomposition of the Ce^{IV} carboxylate. Competition studies presented in Table IV provide a method for determining the relative rates of decarboxylation. If rapid metathesis pertains, the number of Ce^{IV} linkages to carboxylate is controlled by the relative concentrations of the component acids. In agreement with this, the last column in Table IV shows that selectivity to decarboxylation is fairly constant over a range of acid ratios. There are experimental limitations inherent in a highly accurate analysis of a complex mixture of products.[31] Within these bounds we conclude that pivalic, isobutyric, and *n*-butyric acids show no differences in rates of *photochemical* decarboxylation.

If this conclusion is correct, the photochemical homolysis of Ce^{IV} carboxylates derives little help from the alkyl moiety. This is in contrast to the thermal homolysis of Pb^{IV},[31c] Co^{III},[10] and Mn^{III} carboxylates,[32] which show decreasing rates in the order pivalate > isobutyrate > *n*-butyrate. Multibond cleavages have been proposed in the latter cases.[31c]

We postulate that the photochemical homolysis[33] of Ce^{IV} carboxylates proceeds *via* acyloxy radicals, which are known to fragment rapidly.[34] The Ce^{IV} carboxylate

$$Ce^{IV}O_2CR \xrightarrow{h\nu} Ce^{III} + \cdot O_2CR \qquad (8)^{35}$$

$$RCO_2\cdot \xrightarrow{\text{fast}} R\cdot + CO_2 \qquad (9)$$

bond strength has not been measured, but it is undoubtedly less than 80 kcal/mol intrinsic in irradiation at 3500 Å. Activation energies for thermolyses of the related Co^{III} and Mn^{III} carboxylates are less than 40 kcal/mol.[10,32] We think that irradiation at 3500 Å provides sufficient energy for the simple homolysis of Ce^{IV} carboxylate, and the driving force from multibond cleavage is not required. A similar photochemical process probably obtains in the photolysis of Tl^{III} carboxylates.[23]

The quantum yields for the homolysis of Ce^{IV} carboxylates are significantly higher than those obtained in aquocerium(IV) complexes.[4] There is reasonable agreement with values obtained from ceric ammonium nitrate in glacial acetic acid.[6] In the latter case, however, there is ambiguity as to the Ce^{IV} species extant in solution. Extensive involvement of nitrate in addition to acetate in the photochemical process(es) complicates that issue immensely.[36]

The minor variation in ϕ_{CO_2} for the photochemical decarboxylation of Ce^{IV} pivalate, isobutyrate, and *n*-butyrate generally parallels the relative rates presented in Table IV. There are several possible explanations for ϕ_{CO_2} to be a little greater than 1 (*cf.* pivalate).[37,38] A photoinduced decarboxylation of the type represented in eq 10 or other short-chain processes may occur.[39]

$$R\cdot + Ce^{IV}O_2CR \longrightarrow RCe + RCO_2\cdot \text{ etc.} \qquad (10)$$

Alternatively, the high quantum yields obtained with relatively concentrated solutions (0.1 *M*) may be due to associated Ce^{IV} species[26,29] which undergo multiple decarboxylation for each photon absorbed. The slight decrease in ϕ_{CO_2} with dilution (0.01 *M*) is consistent with the dissociation of Ce^{IV} aggregates.

The *thermal* decarboxylation of Ce^{IV} carboxylates in carboxylic media is a slow process. Moreover, Ce^{IV} is not completely reduced, as shown in Table V, even after prolonged heating. The formation of μ-oxocerium(IV) complexes, which are thermally stable, has been observed in glacial acetic acid.[40,41]

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(29) (a) The degree of association of Ce^{IV} does not materially affect our basic arguments (*vide infra*). (b) Studies are in progress.

(30) Problems associated with these types of oxidations have been discussed previously.[23,31]

(31) (a) J. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965); J. Kochi, J. Bacha, and T. Bethea, *ibid.*, **89**, 6538 (1967); J. Kochi, R. Sheldon, and S. Lande, *Tetrahedron*, in press.

(32) J. Anderson, unpublished results.

(33) (a) A variety of photoinduced redox reactions are known; (b) F. Feigl, *J. Chem. Educ.*, **21**, 479 (1944); (c) E. Wehry, *Quart Rev.* (London), **21**, 213 (1967); (d) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 654 ff; (e) J. Kochi, *J. Am. Chem. Soc.*, **84**, 2121 (1962); (f) Martin, *et al.*,[6] have coined the term "ligand-sensitization" to describe this type of internal oxidation–reduction process.

(34) (a) M. Szwarc, "Peroxide Mechanisms," J. Edwards, Ed., Interscience Publishers, New York, N. Y., 1962. (b) Aroyloxy radicals decarboxylate much slower. (c) There is recent evidence for the existence of acetoxy radicals during decomposition of acetyl peroxide [J. Martin and J. Taylor, *J. Am. Chem. Soc.*, **89**, 6904 (1967)].

(35) In the following discussion the coordination around cerium will only be included if pertinent to the discussion.

(36) (a) Martin, *et al.*,[6] proposed 11 steps to rationalize the products from the photoinduced reduction of ceric ammonium nitrate in glacial acetic acid. Of these, nine steps directly or indirectly involve the participation of the nitrate moiety. (b) The presence of NO_3 radical in the photolysis of Ce(IV) nitrate in aqueous solution has been shown.[8]

(37) (a) The well-known ferrioxalate actinometer also shows $\phi_{CO_2} > 1$. An induced reduction of Fe^{III} has been suggested.[38]

(38) (a) J. Lee and H. Seliger, *J. Chem. Phys.*, **40**, 519 (1964); (b) C. Parker, *Trans. Faraday Soc.*, **50**, 1213 (1954); (c) C. Parker and C. Hatchard, *J. Phys. Chem.*, **63**, 22 (1959).

(39) A similar process has been postulated in the photochemical decarboxylation of Hg^{II} carboxylates [Yu. Ol'dekop and N. Maier, *Zh. Obshch. Khim.*, **30**, 303 (1960); *Chem. Abstr.*, **54**, 22334*f* (1960), and later papers].

(40) D. Patnaik and J. Panda, *Current Sci.* (India), **25**, 287 (1956); **26**, 355 (1957); *J. Indian Chem. Soc.*, **33**, 877 (1955).

(41) *Cf.* also J. Seaton, F. Sherif, and L. Audrieth, *J. Inorg. Nucl. Chem.*, **9**, 222 (1959); T. Moeller, V. Galasyn, and J. Xavier, *ibid.*, **15**, 259 (1960).

In the presence of *strong acids*, a dramatic increase in the rate of decarboxylation of $\mathrm{Ce^{IV}}$ carboxylate occurs (Table VI). Alkyl radicals are still the principal intermediates, since they can be trapped (*vide infra*). There is no evidence that a two-equivalent transformation, as in eq 11, applies under these conditions.[42]

$$\mathrm{Ce^{IV}O_2CR} \overset{\mathrm{H^+}}{\not\longrightarrow} \mathrm{Ce^{II}} + \mathrm{R^+} + \mathrm{CO_2} \qquad (11)$$

The enhancement in rate of thermal decarboxylation of $\mathrm{Ce^{IV}}$ carboxylates by strong acids has also been noted with other metal carboxylates derived from $\mathrm{Pb^{IV}}$, $\mathrm{Mn^{III}}$, $\mathrm{Co^{III}}$, and $\mathrm{Tl^{III}}$.[10,23,31,32,43] We believe that this general phenomenon is associated with *ionization* of the metal carboxylate induced by acids.[44] An example of protonolysis is given by eq 12. The cationic metal complex is coordinatively unsaturated[10] and more likely to undergo reduction than its neutral counterparts. The facile decarboxylation (eq 13)[45] and oxidation of alkyl radicals (*vide infra*) are attributed to these charged species. The photochemical decarboxylation of $\mathrm{Ce^{IV}}$ carboxylates is also aided by strong acids (column 3, Table III). Unfortunately, competitive decarboxylation of acids was not examined in the presence of strong acids due to difficulties with quantitative analysis of products.

$$\mathrm{M(O_2CR)}_n + \mathrm{H^+} \rightleftharpoons \mathrm{M(O_2CR)}_{n-1}{}^+ + \mathrm{RCO_2H} \qquad (12)$$

$$\mathrm{Ce^{IV}(O_2CR)_3{}^+} \longrightarrow \mathrm{Ce^{III}(O_2CR)_2{}^+} + \mathrm{RCO_2\cdot}\ \text{etc.} \qquad (13)$$

It is interesting to note that the $\mathrm{Ce^{IV}}$–$\mathrm{Ce^{III}}$ oxidation potential in aqueous solution is quite dependent on the anionic species present.[46] The decrease in this value from perchlorate, nitrate, sulfate, to chloride has been attributed to anation. The high acid concentration required for $\mathrm{Ce^{IV}}$ in aqueous solution may allow for the formation of metastable intermediates.[47]

Alkyl Radicals as Intermediates. The formation of alkyl radicals as prime intermediates in the photochemical and thermal decarboxylation of $\mathrm{Ce^{IV}}$ carboxylates can be shown by trapping experiments. Propane, which is a major product from the decarboxylation of $\mathrm{Ce^{IV}}$ *n*-butyrate, is completely quenched by catalytic amounts of $\mathrm{Cu^{II}}$ (Table III). $\mathrm{Cu^{II}}$ is not directly involved in the decarboxylation step, since it has little effect on the rate.[48] It has been shown that alkyl radicals are oxidized by $\mathrm{Cu^{II}}$ at very fast rates.[9,49a]

$$\mathrm{CH_3CH_2CH_2\cdot} + \mathrm{Cu^{II}} \longrightarrow \mathrm{CH_3CH{=}CH_2} + \mathrm{H^+} + \mathrm{Cu^{I}} \qquad (14)$$

The effective scavenging of alkyl radicals by $\mathrm{Cu^{II}}$ has been demonstrated in a number of cases.[14] The rapid reoxidation[49c] of $\mathrm{Cu^{I}}$ by $\mathrm{Ce^{IV}}$ enables the use of catalytic amounts of $\mathrm{Cu^{II}}$. Under these conditions the stoichiometry of the decarboxylation is given cleanly by eq 16.

$$\mathrm{Cu^{I}} + \mathrm{Ce^{IV}} \longrightarrow \mathrm{Cu^{II}} + \mathrm{Ce^{III}} \qquad (15)$$

$$\mathrm{2(PrCO_2)_4Ce^{IV}} \xrightarrow{\mathrm{Cu^{II}}} \mathrm{2(PrCO_2)_3Ce^{III}} + \mathrm{PrCO_2H} + \mathrm{CO_2} + \mathrm{CH_3CH{=}CH_2} \qquad (16)$$

The decarboxylation of $\mathrm{Ce^{IV}}$ pivalate in pivalic acid yields only traces of isobutane (Table I). Addition of hydrogen donors such as chloroform (Table III) or isobutyric acid (Table IV) causes substantial increases in isobutane. In the latter case, isobutane increases linearly with the concentration of the hydrogen donor compared to isobutylene and *t*-butyl esters (Figure 2).

$$\mathrm{(CH_3)_3C\cdot} + \mathrm{SH} \longrightarrow \mathrm{(CH_3)_3CH} + \mathrm{S\cdot} \qquad (17)$$

$$\mathrm{SH} = \mathrm{CHCl_3},\ \mathrm{C_3H_7CO_2H}$$

The decarboxylation of $\mathrm{Ce^{IV}}$ butyrate induced by acids yields propylene and propyl esters principally. The presence of chloroform will also divert all the propyl radicals to propane (Table III).

$$\mathrm{CH_3CH_2CH_2\cdot} + \mathrm{CHCl_3} \longrightarrow \mathrm{CH_3CH_2CH_3} + \mathrm{\cdot CCl_3} \qquad (18)$$

Oxygen also intercepts alkyl radicals during the decarboxylation of $\mathrm{Ce^{IV}}$ carboxylates (Tabel III). The *t*-butyl radicals from pivalic acid are converted by oxygen to di-*t*-butyl peroxide, *t*-butyl alcohol, and acetone. The latter are well-established products from *t*-butylperoxy radicals.[50]

$$\mathrm{(CH_3)_3C\cdot} + \mathrm{O_2} \longrightarrow \mathrm{(CH_3)_3CO_2\cdot} \qquad (19)$$

$$\mathrm{2\,(CH_3)_3CO_2\cdot} \longrightarrow \mathrm{O_2} + \mathrm{(CH_3)_3COOC(CH_3)_3} \qquad (20)$$

$$\mathrm{2\,(CH_3)_3CO_2\cdot} \longrightarrow \mathrm{O_2} + \mathrm{2\,(CH_3)_3CO\cdot}\ \text{etc.} \qquad (21)$$

Under high oxygen pressure, carbon dioxide, *t*-butyl alcohol, di-*t*-butyl peroxide, and acetone are formed in yields far in excess of the $\mathrm{Ce^{IV}}$ charged. No doubt the cerium complexes are catalytic, and a reaction which regenerates $\mathrm{Ce^{IV}}$ from $\mathrm{Ce^{III}}$ is required. Three routes can be considered.

$$\mathrm{Ce^{III}} + \mathrm{O_2} \longrightarrow \mathrm{Ce^{IV}} + \mathrm{O_2\cdot^-} \qquad (22)$$

$$\mathrm{Ce^{III}} + \mathrm{(CH_3)_3CO\cdot} \longrightarrow \mathrm{Ce^{IV}OC(CH_3)_3} \qquad (23)$$

$$\mathrm{Ce^{III}} + \mathrm{(CH_3)_3COO\cdot} \longrightarrow \mathrm{Ce^{IV}OOC(CH_3)_3} \qquad (24)$$

Although autoxidation of $\mathrm{Ce^{III}}$ is possible (eq 22),[51] it cannot contribute under our conditions since decarboxylation of pivalic acid cannot be photochemically induced by $\mathrm{Ce^{III}}$ at 30°. *t*-Butylperoxy and *t*-butoxy

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[42] However, W. Trahanovsky and L. Young [*J. Org. Chem.*, 31, 2033 (1966)] have recently proposed a direct $\mathrm{Ce^{IV}}$–$\mathrm{Ce^{II}}$ transformation in the oxidation of toluenes.

[43] S. Lande, unpublished studies.

[44] (a) Until $\mathrm{Ce^{IV}}$ species in solution are identified, the specific ionization cannot, of course, be elaborated. Binuclear as well as mononuclear and polynuclear $\mathrm{Ce^{IV}}$ cations may be involved. For simplicity we represent these species as simple cations. (b) If carboxylates are bidentate in these complexes (as they often are), then protonation may simply involve detachment of one oxygen atom from $\mathrm{Ce^{IV}}$ without ionization.

[45] The *thermolysis of* $\mathrm{Ce^{IV}}$ carboxylates may proceed *via* a two-bond cleavage to form alkyl radicals directly.

[46] (a) E. Wadsworth, F. Duke, and C. Goetz, *Anal. Chem.*, **29**, 1824 (1957). (b) No perchlorate complexes of $\mathrm{Ce^{IV}}$ have been found [R. Moore and R. Anderson, *J. Am. Chem. Soc.*, **67**, 167 (1945); M. Jones, *et al.*, *ibid.*, **83**, 2039 (1961)].

[47] The problem is more severe in water than nonaqueous solvents such as carboxylic acid due to the leveling effect of water on acids.

[48] (a) Moreover, under our conditions $\mathrm{Cu^{II}}$ carboxylates show negligible absorption at 3500–3600 Å, and cannot be involved in energy transfer processes. (b) $\mathrm{Cu^{II}}$ carboxylates are not particularly prone to undergo photochemical reduction even at lower wavelengths. (c) Qualitative, based on time required for half-completion of reaction.

[49] (a) J. Kochi, A. Bemis, and C. Jenkins, *J. Am. Chem. Soc.*, **90**, 4616 (1968); (b) A. MacLachlan, *J. Phys. Chem.*, 71, 4132 (1967); (c) A. Sykes, *Advan. Inorg. Chem. Radiochem.*, 10, 206 (1967), for analogous cases.

[50] (a) P. Bartlett and T. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963); (b) A. Factor, C. Russell, and T. Traylor, *ibid.*, **87**, 3692 (1965); (c) P. Bartlett and P. Günther, *ibid.*, **88**, 3288 (1966); (d) see also J. Barnard and A. Cohen [*Trans. Faraday Soc.*, **65**, 396 (1968)] for methanol from methyl radicals and oxygen (Table III).

[51] For example, M. Mendelsohn, E. Arnett, and H. Freiser, *J. Phys. Chem.*, **64**, 660 (1960).

radicals are known to oxidize Ce^{III}.[52] In addition, *t*-butyl hydroperoxide formed in eq 24 also undergoes catalytic decomposition by cerium salts.[53] The radical chain sequences 8–9 (13) and 19–24 constitute an important part of the autoxidative decarboxylation of pivalic acid promoted by Ce^{IV}. A similar catalytic process has also been observed in the thermal decomposition of Co^{III} and Mn^{III} carboxylates in the presence of oxygen.[10,32]

Oxidation of Alkyl Radicals by Ce^{IV}. The fate of the alkyl radical is largely independent of the decarboxylation step (eq 8 and 9). Alkanes (RH) arise by hydrogen transfer from the solvent. Alkenes[54] and esters (R_{ox}) result from oxidation of alkyl radicals by Ce^{IV}. The molar ratio R_{ox}/RH of oxidation products compared to alkane represents a measure of the relative rates of oxidation and reduction of alkyl radicals under experimental conditions.[31,40]

In competitive decarboxylations of a pair of acids, both alkyl radicals are generated in the same milieu. The oxidation and reduction of *t*-butyl radicals (*t*-Bu_{ox}/*t*-BuH) from pivalic acid and various amounts of either isobutyric or *n*-butyric acid are shown in Figure 2. The slopes and intercepts in the figure indicate that acids decline as hydrogen donors in the expected order isobutyric > *n*-butyric > pivalic.[55]

The following processes are applicable to *t*-butyl and isopropyl radicals from the competitive decarboxylation of pivalic and isobutyric acids.

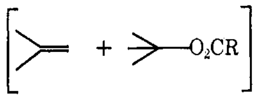
hydrogen transfer

$$(CH_3)_3C\cdot + (CH_3)_2CHCO_2H \xrightarrow{k_H} (CH_3)_3CH + (CH_3)_2\dot{C}CO_2H \quad (25)$$

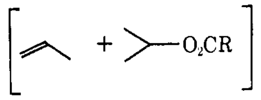
$$(CH_3)_2CH\cdot + (CH_3)_2CHCO_2H \xrightarrow{k_H'} CH_3CH_2CH_3 + (CH_3)_2\dot{C}CO_2H \quad (26)$$

oxidation

$$(CH_3)_3C\cdot + Ce^{IV} \xrightarrow[RCO_2H]{k_{OX}}$$

 $+ H^+ + Ce^{III}$ (27)

$$(CH_3)_2CH\cdot + Ce^{IV} \xrightarrow[RCO_2H]{k_{OX}}$$

 $+ H^+ + Ce^{III}$ (28)

The values of R_{ox}/RH are given in Table IV. Interestingly, the variation of *t*-Bu_{ox}/*t*-BuH parallels *i*-Pr_{ox}/*i*-PrH as the relative amounts of pivalic and isobutyric acids are altered. The value of R_{ox}/RH for *t*-butyl radicals is 40–50 times larger than for isopropyl radicals. The discrepancy of R_{ox}/RH between *t*-butyl and *n*-propyl radicals is even greater, the former being more than 100 times larger than the latter. These values of R_{ox}/RH do not quantitatively reflect rates of oxidation and hydrogen transfer, k_{ox}/k_H. If we assume that hydrogen transfer rates do not vary greatly among these alkyl radicals,[56] we can observe generally that *t*-butyl radicals are oxidized by Ce^{IV} faster than isopropyl or *n*-propyl radicals.

The addition of strong acids to Ce^{IV} carboxylates causes the values of R_{ox}/RH to increase pronouncedly (Tables II and VI). Alkanes are minor products. We attribute the increase in R_{ox} to more efficient oxidation of alkyl radical by Ce^{IV} in the presence of acids. Earlier we formulated positively charged Ce^{IV} carboxylates as being responsible for enhanced rates of decarboxylation (eq 13). We think the same cationic Ce^{IV} species also oxidize alkyl radicals more rapidly than their neutral counterparts. In addition to being more powerful oxidants, they are coordinatively unsaturated.[57a] The latter could be important if oxidation occurred *via* an inner sphere complex.[57b] In such an event the rate

$$R\cdot + Ce^{IV} \rightleftarrows [RCe] \quad (29)$$

of ligand substitution on the Ce^{IV} nucleus may actually be the step which controls the oxidation of alkyl radicals.[58] The extent of coordination of Ce^{IV} would influence the rate of substitution.

Heterolysis of the alkylcerium intermediate leads to Ce^{III} and an alkyl carbonium ion. Subsequent loss of

$$[RCe] \longrightarrow Ce^{III} + R^+ \text{ etc.} \quad (30)$$

a proton or solvation of the carbonium ion would provide the observed alkenes and esters.[59] Differing rates of oxidation of various radicals are attributed to reversibility in the association step (reaction 29) and the stability of the carbonium ion in the heterolysis (30).[60]

The formation of isopropyl esters from the decarboxylation of Ce^{IV} *n*-butyrate is consistent with carbonium ion intermediates. However, we also observe significant amounts of *n*-propyl esters. It is possible that these arise *via* direct substitution on the inner sphere complex or by ligand transfer processes.[61]

The mechanisms of oxidation of alkyl radicals by other metal oxidants[62] such as Cu^{II}, Pb^{IV}, Co^{III}, and Mn^{III} bear strong resemblance to Ce^{IV}. At this juncture, it is interesting to note that rates of oxidation of alkyl radicals by various metal oxidants seem to bear no strong relationship to the oxidation potential of the metal couple. Thus, Pb^{IV}, Co^{III}, Mn^{III}, and Ce^{IV} are all more potent oxidizing agents than Cu^{II}, yet the latter appears to be a more effective scavenger of alkyl radicals by at least a factor of 100. Further quantitative measurements are required before this important anomaly can be resolved.[63]

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(52) *Cf.* W. de Klein and E. Kooyman, *J. Catal.*, **4**, 626 (1965).

(53) Reference 1, pp 267–269.

(54) We could find no alkyl dimers under our experimental conditions and concluded that bimolecular reactions of alkyl radicals are absent. We discount disproportionation as a route to alkene. *Cf.* ref 23.

(55) K. Itoh, S. Sakai, and Y. Ishii, *Tetrahedron*, **22**, 509 (1966).

(56) J. Kerr and A. Trotman-Dickenson, *Progr. Reaction Kinetic*, **1** 107 (1961).

(57) (a) There are a variety of ways in which strong acids can induce the formation of coordinatively unsaturated Ce^{IV} species. *Cf.* a discussion with Co^{III} complexes.[10] (b) The designation of the oxidation state of cerium in this complex has been deliberately omitted.

(58) This is particularly true for alkyl radicals since they have alternative low-energy pathways for reaction.

(59) (a) C. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963; D. Banthorpe, "Elimination Reactions," Elsevier Publishing Co., New York, N. Y., 1963. (b) It is possible that some alkane may also arise through this intermediate by protonolysis. Studies are in progress to examine this possibility.

(60) *Cf.* the mechanism of oxidation of alkyl radicals by Cu^{II} complexes.[49a]

(61) We expect an *n*-propyl cation from the heterolysis (eq 30) to rearrange completely to the isopropyl cation. Further studies are in progress to delineate these processes further.

(62) J. Kochi, *Science*, **155**, 415 (1967).

Conclusions

Studies of the photochemical and thermal decomposition of Ce^{IV} carboxylates provide unequivocal evidence for one-electron oxidation of organic species. The mechanism of decarboxylation of simple acids can be related to the role of oxalates[64] and other functional groups in oxidation–reduction reactions.

The decarboxylation of Ce^{IV} carboxylates also provides a method for the efficient production of a variety of alkyl radicals. Factors which determine the rates of oxidation of alkyl radicals by Ce^{IV} merit further study. The marked effect of strong acids in altering the properties of the Ce^{IV} oxidant is a general phenomenon which should be applicable to other substrates.

Experimental Section

Materials. All carboxylic acids were purified by distillation. Chloroform was redistilled in an atmosphere of nitrogen before use. Di-*t*-butyl peroxide was generously donated by the Shell Chemical Co. All esters were prepared by standard procedures. Pyridine was redistilled from potassium hydroxide before use.

The preparation of ceric acetate has been described elsewhere.[16] The procedure was modified somewhat by washing out the last traces of acetic acid from the ceric acetate with pentane several times before it was placed in a vacuum desiccator over potassium hydroxide. Analysis by ferrous titration indicated 98–99% $Ce(OAc)_4$.

Anal. Calcd for $CeC_8H_{12}O_8$: C, 25.54; H, 3.22. Found: C, 25.41, 25.50; H, 3.37, 3.41.

Thermal Decarboxylations. Aliquots (5 ml) of a 0.1 *M* solution of ceric acetate in the carboxylic acid were decomposed at 80° in glass tubes, sealed tightly with rubber septa, in an oxygen-free atmosphere. In experiments employing a catalyst, it was added to the reaction as the last component prior to removal of oxygen. In the case of perchloric acid catalyzed reactions, which were very fast, the perchloric acid was added after removal of oxygen. In the case of reactions carried out in the presence of added oxygen, solutions were flushed thoroughly with oxygen for 5 min using a hypodermic needle which passed below the surface of the solution.

Photochemical Decarboxylations. The photolytic decarboxylations were carried out in a Rayonet RPR-100 photochemical reactor (The Southern New England Ultraviolet Co.). Four 3500-Å region lamps (3050–4150 Å) or four 2537-Å region lamps were employed. The maximum capacity of the reactor is 16 lamps. Aliquots (5 ml) of a 0.1 *M* solution[65] of ceric acetate in the carboxylic acid were transferred from a standard flask to 40 × 1 cm quartz tubes. The solution and the free space above the solution were purged of oxygen by sweeping with a slow stream of nitrogen or helium for 5–10 min. After the tube was sealed tightly with a rubber septum, it was placed in the photochemical reactor which maintained an ambient temperature of 30 ± 1°. The lamps were arranged in a circular array and the tubes placed 10 cm from the nearest lamp. The progress of the reaction was followed by the disappearance of the yellow ceric color. Upon completion the solutions were colorless.

In the case of the reaction in the presence of added cupric acetate, a solution of cupric acetate in the carboxylic acid was added to the $Ce(OAc)_4$ solution and the above procedure followed. The progress of these reactions was followed by a color change from green to the blue of cupric acetate.

Solutions for competitive decarboxylations were made up by mixing appropriate quantities of solutions of $Ce(OAc)_4$ in the respective acids and carrying out the reactions in the usual manner.

Analytical Procedures. When the reactions were complete, which was usually indicated by the yellow solutions becoming colorless, they were immediately analyzed qualitatively for possible gaseous products. The tubes were then cooled in liquid nitrogen and markers added for quantitative gas analysis. The tubes were allowed to warm to room temperature with vigorous agitation and analyzed for gaseous products. Mixtures containing known amounts of products and markers were analyzed in the same way to obtain calibration factors. Pressure was then released from the tubes and a marker for ester analysis added; the solutions were made up to 25 cc with glacial acetic acid. Aliquots (5 ml) of this solution were taken up in ether (5 ml) and washed three times with saturated sodium bicarbonate solution to remove excess carboxylic acid. The ether solution was analyzed for the remaining products. Solutions of products of known concentrations were worked up in the same way. The acetic acid reaction mixture was analyzed directly for methyl acetate (the usual work-up was not feasible due to methyl acetate being too water soluble). Acetone, *t*-butyl alcohol, and di-*t*-butyl peroxide were analyzed directly without the above work-up.

Gas chromatographic analyses of gaseous products were performed on Case-constructed instruments, equipped with thermal conductivity detectors. Other analyses were performed on instruments with hydrogen flame ionization detectors: Varian Aerograph Model 1200 and Aerograph HiFy Model 600. The following are the conditions used in determining yields of products (product, marker, column, temperature): carbon dioxide, ethane, 2-ft Porapak Q, room temperature; methane, ethane, 2-ft Porapak Q, room temperature; fluoroform, ethane, 2-ft Porapak Q, room temperature; propane, isobutane, 15-ft 30% Dowtherm on firebrick, room temperature; propane, isobutane, 15-ft 30% Dowtherm on firebrick, room temperature; isobutane, *n*-butane, 15-ft 30% Dowtherm on firebrick, room temperature; methyl acetate, isopropyl acetate, 10-ft FFAP, 85°; isopropyl acetate, *n*-butyl acetate, 8-ft DEGS, 90°; *n*-propyl acetate, *n*-butyl acetate, 8-ft DEGS, 90°; *n*-propyl-*n*-butyrate, *n*-butyl acetate, 8-ft DEGS, 90°; isopropyl *n*-butyrate, *n*-butyl acetate, 8-ft DEGS, 90°; isopropyl isobutyrate, *n*-butyl acetate, 8-ft DEGS, 90°; *t*-butyl acetate, *n*-butyl acetate, 6-ft Morflex, 90°; *t*-butyl isobutyrate, *n*-butyl acetate, 6-ft Morflex, 90°; acetone, *n*-hexane, 10-ft FFAP, 90°; di-*t*-butyl peroxide, *n*-hexane, 10-ft FFAP, 90°; *t*-butyl alcohol, *n*-hexane, 10-ft FFAP, 90°; 2,4,4-trimethylpentene, *n*-hexane, 10-ft FFAP, 90°.

Oxygen Bomb Reaction. The heavy-walled glass reaction vessel consisted of a 100-ml bulb fused to a glass pipe terminated with an O-ring seal. The reactor was charged by pipeting in a standard solution of $Ce(OAc)_4$ in pivalic–acetic acid 96:4 v/v. A stainless steel cap equipped with a needle valve was attached to the vessel *via* a split steel collar. The reactor was pressured with 40 psig of oxygen, the cap valve closed, and the solution magnetically stirred. The solution was protected from the steel cap and valve by a Teflon disk with a minute hole to permit the introduction of oxygen. The bomb was then placed in the photochemical reactor and the solution photolyzed, at 3500 Å using four lamps, until the solution turned colorless. The gases were then vented into a mercury-filled gas buret and analyzed for carbon dioxide using ethane as the internal standard. The solution was analyzed directly for acetone, *t*-butyl alcohol, and di-*t*-butyl peroxide, using *n*-hexane as an internal standard.

Ceric Isobutyrate and Ceric Pivalate. A mixture of ceric acetate (7.52 g) and isobutyric acid (40 g) was stirred at 80° *in vacuo* (water pump). The ceric acetate dissolved to give an orange solution and acetic acid distilled out and was collected. When distillation of acetic acid was complete the mixture was allowed to cool. The product separated as an orange-yellow solid and was collected, washed with pentane, and dried *in vacuo* to give ceric isobutyrate (5.7 g, 58%), 98% $Ce(O_2CCH(CH_3)_2)_4$ by ferrous titration. The pmr spectrum of the product (in $CHCl_3$) showed a doublet at τ 8.83 (J_{H-H} = 7 cps).

Similarly, ceric pivalate (3.3 g, 30%) was obtained as a yellow solid from ceric acetate (7.52 g) and pivalic acid (40 g) and was shown to be 95% $Ce(O_2CC(CH_3)_3)_4$ by ferrous titration. The pmr spectrum of the pivalate (in $CHCl_3$) showed a singlet at τ 8.78.

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(63) Thermodynamic trends, of course, do not necessarily have to coincide with kinetic factors, despite large differences involved. Such would be particularly true if rates of ligand substitution and not oxidation were rate determining.

(64) (a) For example, the recent observation by Taube and Andrade shows that only one CO_2 from the Ce^{IV} oxidation of methyl oxalate is labeled with oxygen from water, whereas both CO_2's from dimethyl oxalate are so labeled [*Inorg. Chem.*, **5**, 495 (1966)]. This is in accord with our studies, if one assumes that the methoxycarbonyl radical is oxidized by Ce^{IV} and that dimethyl oxalate is hydrolyzed to methyl oxalate by Ce^{IV} or Ce^{III} before oxidation (eq i and ii). (b) There are,

$$CH_3O_2CCO_2H + Ce^{IV} \longrightarrow CO_2 + Ce^{III} + CH_3O_2C\cdot \xrightarrow[H_2O^*]{Ce^{IV}} CH_3OH + CO_2^* + Ce^{III} \quad \text{(i)}$$

$$CH_3O_2CCO_2CH_3 + H_2O\cdot \xrightarrow{Ce^{n+}} CH_3OH + CH_3O_2CCO_2^*H \quad \text{etc.} \quad \text{(ii)}$$

however, some anomalous observations.[15]

(65) It was sometimes necessary to warm the mixtures with efficient stirring to effect complete solution, but it was shown that no reaction took place during warming.

Quantum Yield Measurements. The reaction vessel consisted of a 1 × 4 cm Pyrex cell fused to a glass pipe containing a gas-tight stopcock. The solution to be irradiated (4 cc) was placed in the cell and the apparatus evacuated. The reaction was allowed to proceed to 2–3% conversion and then ethane (marker) was introduced, using a gas-tight microsyringe, *via* a rubber septum which sealed the glass tube above the stopcock. The yield of carbon dioxide was determined by gas chromatography. Ferrioxalate actinometry was used as the reference for quantum yield measurements. A 1 × 0.5 cm window in the reaction cell was irradiated using a medium-pressure mercury vapor lamp and isolating the desired light with a Corning 7-37 glass filter, which was transparent to light in the region 3180–3860 Å (maximum transmission at 3600 Å). There was a dark reaction under these conditions but this only accounted for approximately 2% of the total reaction.

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Solvation Enthalpies and Rates of Nucleophilic Displacement of Alkali Halides in Dimethyl Sulfoxide

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Abstract: Enthalpies of solution have been measured for LiCl, LiBr, LiI, KBr, and KI in DMSO. From these, the values in water, and lattice energies, enthalpies of solvation in both solvents have been calculated. Contrary to a number of suggestions, the solvation of halide ions in DMSO is $Cl^- > Br^- > I^-$, the same as in water. The rates of displacement on *n*-propyl tosylate by halides in aqueous DMSO are in the order $I^- > Br^- > Cl^-$, while in DMSO the opposite order is observed. The reversed nucleophilic order is attributed to the smaller difference in halide solvation in DMSO than in water. This would rationalize the observed rates if one assumes the order of nucleophilicities of the unsolvated ions toward *n*-propyl tosylate to be $Cl^- > Br^- > I^-$.

In recent years a number of authors[2–5] have observed and reported that dipolar aprotic solvents such as DMSO accelerate the rates of certain nucleophilic displacement reactions. Miller and Parker[3] have also shown that, in going from protic to dipolar aprotic solvent, the reaction rates of small nucleophiles are increased to a greater extent than are the rates of larger ones. It has been suggested that in dipolar aprotic solvents anions are poorly solvated.[2,6] This idea has been used[2,3] to explain the rate enhancement under the supposition than an unsolvated nucleophile should be more reactive than a solvated one from which solvent molecules must be removed before reaction can occur.

Arnett and McKelvey[7] have indicated, through estimated single ion enthalpies of transfer from water to DMSO, that water is a better solvating medium for small anions than for large ones, and that the degree of solvation of the halide ions by water lies in the order $Cl^- > Br^- > I^-$. The enthalpies of transfer (water to DMSO) are in the order I^- (exothermic) < zero < $Br^- < Cl^-$, suggesting that I^- actually undergoes a solvation increase in the transfer.

The idea that large, polarizable anions should be most solvated in DMSO has led to the alternative suggestion[2,4] that the increased rate of nucleophilic displacement may be due to preferential solvation of the $\mathrm{S_N2}$ transition state, which would lower the energy of the transition state, and the activation energy. Our present study casts some doubt on this viewpoint. While we believe that this idea and Arnett's assignment of equal enthalpies of transfer for $(C_6H_5)_4As^+$ and $(C_6H_5)_4B^-$ ions as a basis for single ion enthalpies both seem quite reasonable, we find no compelling evidence that large anions are, in fact, more strongly solvated than small anions in dipolar aprotic solvents. Measurements of solvation enthalpies in DMSO presented below suggest that the opposite is correct. Alternative explanations for a wide variety of rate, equilibrium, and thermodynamic observations can be based solely on the viewpoint that small anions are more strongly solvated in protic solvents than are large anions, and both the degree of solvation and the difference are diminished in dipolar aprotic solvents.

It has been demonstrated[8] that picric acid is stronger than HBr in DMSO while the reverse holds true in water. This is in agreement with the idea[2,4] that large anions are poorly solvated in water but are more solvated in dipolar aprotic solvents than are small ones. In water the bromide ion may be stabilized through solvation, leading to strong dissociation of the acid, while in DMSO there may be less dissociation due to less anion solvation. The picrate ion may be less solvated in water than is bromide but more solvated in DMSO, and

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(1) Author to whom inquiries should be directed. Support of this work by the Robert A. Welch Foundation (Grant E-136) is gratefully acknowledged.

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