(84.6%) of crude crystalline substance was obtained, which was recrystallized from water to give 1.1 g (59.3%) of **6**. This compound gave an identical ir spectrum and uv absorption pattern with those of **6** derived from 4-*N*-oxide **2**, mp 167–170°, $[\alpha]^{14}\text{D}$ −65.4° (after 24 hr) (*c* 1.0, water).

Anal. Calcd for $C_8H_{12}N_2O_4$: C, 47.99; H, 6.04; N, 14.00. Found: C, 48.25; H, 6.25; N, 14.20.

Pyrazine-2-carboxylic Acid (7).—To a solution of 2.2 g of **6** in 400 ml of water, 6.0 g of potassium permanganate was added in small portions with stirring at 90° for 5 hr. After addition of a small volume of methanol for digesting the excess of potassium permanganate, the precipitate was filtered off and washed with hot water. The filtrate and washings were combined and passed through a column of Amberlite IR-120 (H^+). Concentration of this effluent *in vacuo* and recrystallization of the residue from water yielded 760 mg (55.8%), mp 225° dec, ir (Nujol) 1710 cm^{-1} (C═O).

Anal. Calcd for $C_5H_4N_2O_2$: C, 48.39; H, 3.25; N, 22.28. Found: C, 48.40; H, 3.49; N, 22.28.

2-(D-*arabino*-Tetraacetoxybutyl)pyrazine 1-*N*-Oxide (11).—A mixture of **10** (3 g), acetic anhydride (50 ml), and pyridine (50 ml) was kept for 15 hr at room temperature and poured into ice water. The mixture was extracted with chloroform and the extract was treated as described for **3**.[9] The crystals from the chloroform extract were washed with ether and recrystallized with ethanol to give 4.1 g (76.8%) of **11**: mp 97°; $[\alpha]^{15}\text{D}$ −30.5° (*c* 1.0, methanol); ir (Nujol) 1745 (C═O), 1600, 1310 cm^{-1} (N → O); uv max (methanol) 224, 269 mμ; nmr ($CDCl_3$) τ 8.80, 7.95, 7.88, 7.78 (s, 3 H, AcO-1′, AcO-2′, AcO-3′, and AcO-4′), 5.74 (m, 2 H, $J_{4'a4'b}$ = 12.5 Hz, H-4′), 4.66 (m, 1 H, $J_{3'4'a}$ = 3.0, $J_{3'4'b}$ = 4.5 Hz, H-3′), 4.24 (q, 1 H, $J_{2'3'}$ = 9.0 Hz, H-2′), 3.43 (d, 1 H, $J_{1'2'}$ = 2.5 Hz, H-1′), 1.89 (q, 1 H, H-6 or H-5), 1.57–1.64 (m, 2 H, H-5 or 6 and H-3).

Anal. Calcd for $C_{16}H_{20}N_2O_9$: C, 49.98; H, 5.24; N, 7.29. Found: C, 49.70; H, 5.13; N, 7.18.

2-(D-*arabino*-Tetraacetoxybutyl)pyrazine (12).—A mixture of **6** (500 mg), pyridine (20 ml), and acetic anhydride (20 ml) was kept at 37° for 20 hr. From the reaction mixture tetra-*O*-acetate was extracted with chloroform and the extract was treated as described for **3**[9] to give 600 mg (61.5%) of **12**: mp 110–111°; $[\alpha]^{15}\text{D}$ −1.22° (after 48 hr) (*c* 1.0 methanol); ir (Nujol) 1740 mμ (C═O); nmr ($CDCl_3$) τ 8.11, 7.97, 7.90, 7.78 (s, 3 H, AcO-1′, AcO-2′, AcO-3′, and AcO-4′), 5.74 (m, 2 H, $J_{4'a4'b}$ = 12.0 Hz, H-4′), 4.71 (m, 1 H, $J_{3'4'a}$ = 2.5, $J_{3'4'b}$ = 4.0 Hz, H-3′), 4.31 (m, 1 H, $J_{2'3'}$ = 9.0 Hz, H-2′), 3.84 (d, 1 H, $J_{1'2'}$ = 2.5 Hz, H-1′), 1.43–1.50 (m, 3 H, H-3, 5, or 6).

Anal. Calcd for $C_{16}H_{20}N_2O_8$: C, 52.17; H, 5.47; N, 7.61. Found: C, 52.13; H, 5.41; N, 7.51.

Registry No.—**2**, 21537-56-4; **4**, 34546-42-4; **5**, 34546-43-5; **6**, 34546-44-6; **7**, 98-97-5; **10**, 34546-45-7; **11**, 34546-46-8; **12**, 34546-47-9.

Decarboxylation of Some Thallium(III) Carboxylates. A Mass Spectral Study

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Many heavy metal alkyl and aryl derivatives have been prepared by decarboxylation of the appropriate carboxylates.[3] The photolysis of primary, secondary, and tertiary carboxylic acids in the presence of thallium(III) has been studied, and the products are thallium(I) carboxylates and organic compounds derived from the radical R·.[4] No other such studies have been reported. Observation of the fragmentation of thallium(III) carboxylates in the mass spectrometer would shed some light on the nature of decarboxylation reactions.

Results and Discussion

Thallium(III) Acetate.—The ion of highest *m/e* value found in the mass spectrum of thallium(III) acetate is the molecular ion, $(CH_3COO)_3Tl^+$. It is clear that one of the major fragmentation pathways from the molecular ion is *via* successive loss of acetate groups and that this is substantiated by the observation of the appropriate metastable peaks (Table I).

TABLE I
MONOISOTOPIC MASS SPECTRA OF $(RCOO)_3Tl$ (R = CH_3 AND C_6H_5)

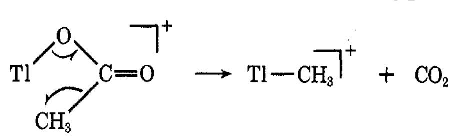
	R = CH_3		R = C_6H_5	
Ion	*m/e*	Rel intensity	*m/e*	Rel intensity
$(RCOO)_3Tl^+$	382	0.1	568	*a*
$(RCOO)_2TlH^+$	324	1.3		
$(RCOO)_2Tl^+$	323	51	447	0.1
$(RCOO)Tl(R)(H)^+$	280	0.1		
$(RCOO)TlR^+$	279	0.2	403	0.2
R_2Tl^+			359	0.2
$(RCOO)Tl^+$	264	0.8	326	8.6
RTl^+	220	0.4	282	19
$TlCO_2^+$	249	6.2	249	6.4
TlO^+	221	0.2		
Tl^+	205	100	205	100

Metastable Transitions

	m/e		
Process	Obsd	Calcd	Neutral fragment lost
	R = CH_3		
323 → 264	∼216	215.8	CH_3COO
264 → 205	159.2	159.2	CH_3COO
	R = C_6H_5[b]		
326 → 282	243.9	243.9	CO_2
403 → 205	104.3	104.3	$C_6H_5COOC_6H_5$

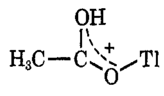
[a] Not observed. [b] Miscellaneous unassigned peak: ∼174.

The formation of methylthallium species is probably associated with a rearrangement of the type



However, the possibility of thermal decarboxylation at the heated ion source cannot be ruled out, but seems less likely. It has previously been shown that the reverse reaction, *i.e.*, the insertion of carbon dioxide into the thallium–carbon bonds of trimethylthallium, does not occur at all at room temperature.[5]

Also present in the spectrum are the ions $(CH_3COO)_2TlH^+$ and $(CH_3COO)Tl(CH_3)H^+$, which are probably thallium hydride species, but the possibility of other structures such as



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[3] G. B. Deacon, *Organometal. Chem. Rev. A*, **5**, 355 (1970).

[4] J. K. Kochi and T. N. Bethea, *J. Org. Chem.*, **33**, 75 (1968).

[5] A. G. Lee, *J. Chem. Soc. A*, 467 (1970).

cannot be excluded. For organothallium(III) compounds, only dimethylthallium phenoxide shows such species in its mass spectrum.[6]

Thallium(III) Benzoate.—The mass spectrum of thallium(III) benzoate (Table I) contains the ions $(C_6H_5COO)_nTl^+$ (n = 1 or 2), although the molecular ion is not observed. Multiplets attributable to species such as $(C_6H_5COO)TlC_6H_5^+$, $(C_6H_5)_2Tl^+$, and $C_6H_5Tl^+$, which are present in low abundance, are formed by elimination of carbon dioxide molecules from the ions $(C_6H_5COO)_nTl^+$ (n = 1 or 2). This is partly justified by the presence of a metastable ion at *m/e* 243.9 which may be related to the process

$$(C_6H_5COO)Tl^+ \longrightarrow C_6H_5Tl^+ + CO_2$$

Carbonation of triphenylthallium in refluxing xylene has been reported to give biphenyl and thallium(I) benzoate.[7]

On summation of the relative abundances of the phenylthallium species, it is apparent that the decarboxylation of thallium(III) benzoate in the mass spectrometer occurs more readily than does that of the acetate.

Thallium(III) Trifluoroacetate.—The molecular ion is absent in the mass spectrum of thallium(III) trifluoroacetate (Table II), which bears little or no resemblance to that of the acetate. The presence of dimeric species such as $(CF_3COO)_3Tl_2^+$ and $(CF_3COO)Tl_2^+$ suggests that the trifluoroacetate is polymeric or, more probably, dimeric in the gas phase.

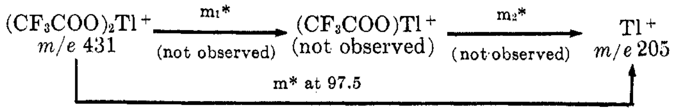
TABLE II

MONOISOTOPIC MASS SPECTRUM OF $(CF_3COO)_3Tl$[a]

m/e	Ion	Rel intensity
749	$(CF_3COO)_3Tl_2^+$	1.2
523	$(CF_3COO)Tl_2^+$	2.6
431	$(CF_3COO)_2Tl^+$	32
410	Tl_2^+	0.8
377[b]	$C_4F_4O_3Tl^+$	28
353[b]	$C_2F_4O_3Tl^+$	10
299	CF_2COOTl^+	4.3
275	$Tl(OF)_2^+$	1.2
249	$TlCO_2^+$	6.0
240	$TlOF^+$	0.9
221	TlO^+	2.2
205	Tl^+	100

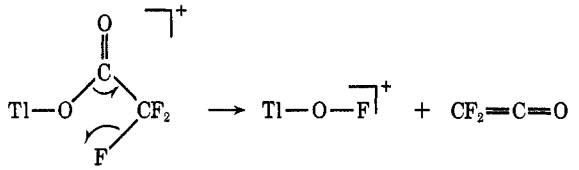
[a] The only metastable ion observed at *m/e* 97.5 corresponds to the process 431 → 205 (calculated *m/e* 97.5) with the loss of two CF_3COO groups. [b] See text.

Consecutive loss of two trifluoroacetate groups from the highly abundant ion, $(CF_3COO)_2Tl^+$, is confirmed by the presence of a metastable ion (m*) at *m/e* 97.5.



No other metastable peaks could be seen in the spectrum.

Another striking feature of the spectrum is the absence of both trifluoromethylthallium and thallium hydride species. The ion at *m/e* 353 would correspond to $(CF_3COO)TlOF^+$, but that at *m/e* 377 is of unknown structure. The formation of $(CF_3COO)TlOF^+$ and other unexpected ions such as $Tl(OF)_2^+$ and $TlOF^+$ may be attributed to a rearrangement of the following type.



All previous attempts to prepare trifluoromethylthallium(III) derivatives have failed.[8]

Experimental Section

Since the complexes are moisture sensitive, all manipulations were performed under a dry atmosphere of nitrogen.

Preparation of the Complexes.—Thallium(III) carboxylates were prepared by refluxing thallium(III) oxide (Johnson Matthey Chemicals) with the appropriate carboxylic acid in the presence of the corresponding acid anhydride.[9-12] Methyl benzoate was used as a solvent in the case of the benzoate. The reaction period ranges from 3 days to a week, until all the oxide had been consumed.

Mass Spectra.—The mass spectra were recorded on A. E. I. MS9 and MS12 spectrometers operating at source pressures of *ca.* 2×10^{-7} Torr, 70 eV ionizing energy, 100 μA ionizing current, resolution of 1000, and 8 kV accelerating voltage. Samples were introduced by direct insertion into the heated ion source (160°). The intensity of the multiplets of the metal-containing ions was normalized to the ^{205}Tl peak. The characteristic isotope pattern was observed for each thallium containing ion.

Registry No.—$(RCOO)_3Tl$ (R = CH_3), 2570-63-0; $(RCOO)_3Tl$ (R = C_6H_5), 14332-12-8; $(CF_3COO)_3Tl$, 23586-53-0.

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[6] A. G. Lee, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 329 (1969).

[7] H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, **61**, 1513 (1939); **62**, 2357 (1940).

[8] A. G. Lee, "The Chemistry of Thallium," Elsevier, London, 1971.

[9] W. O. Rabe and H. Steinmetz, *Chem. Ber.*, **35**, 4447 (1902).

[10] R. Abegg and J. F. Spencer, *Z. Anorg. Allg. Chem.*, **46**, 406 (1905).

[11] A. South and R. J. Ouellette, *J. Amer. Chem. Soc.*, **90**, 7064 (1968).

[12] A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Lett.*, 2423 (1969).