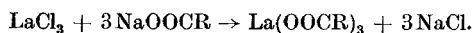


Organic Salts of Samarium

By M. HASAN, B. S. SANKHLA, S. N. MISRA and R. N. KAPOOR*)

The tricarboxylates of samarium have been prepared from the reaction of samarium chloride with sodium salt of the fatty acid (lauric, myristic, palmitic and stearic) in aqueous medium. The synthesis of tricarboxylates was also carried in a nonaqueous medium from the interaction of samarium isopropoxide with acids (acetic propionic butyric, mandelic and salicylic) in different molar ratios. The anhydrous monomeric acetate of samarium was isolated from the reaction of anhydrous samarium chloride with acetic acid, acetic anhydride and their mixture.

There has been a controversy regarding the existence of aluminium acylates for a pretty long time¹⁻⁵). It was the work of MEHROTRA and PANDE⁶)⁷) who isolated these compounds as definite chemical entities. MISRA et al.⁸)⁹) on the other hand have observed that the tervalent elements like lanthanum, cerium(III) praseodymium and neodymium are precipitated almost quantitatively as tricarboxylates when their metal chloride solution is treated with sodium salt of the acid in aqueous medium.



SEATON et al.¹⁰) have claimed the isolation of oxoacetates of the type $(\text{AcO})_2 \cdot \text{M}-\text{O}-(\text{OAc})_2 \cdot 2 \text{ACOH}$ which are converted to the triacetates

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¹) J. W. MCBAINS and W. L. MCLATCHIE, *J. Amer. chem. Soc.* **54**, 3266 (1932).

²) E. EIGENBERGER, *Fett Seifen* **49**, 505 (1940).

³) K. J. MYSEL, *J. Amer. chem. Soc.* **70**, 1053 (1948).

⁴) V. R. GRAY and A. E. ALAXANDER, *J. physic. Chem.* **53**, 23 (1949).

⁵) C. G. MCGEE, *J. Amer. chem. Soc.* **71**, 278 (1949).

⁶) K. C. PANDEY and R. C. MEHROTRA, *J. inorg. nuclear Chem.* **2**, 60 (1956); **4**, 128 (1957).

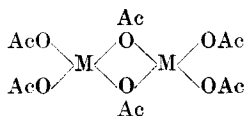
⁷) K. C. PANDEY and R. C. MEHROTRA, *Z. anorg. allg. Chem.* **290**, 87, 95 (1957); *J. prakt. Chem.* **5**, 101 (1957).

⁸) S. N. MISRA, T. N. MISRA and R. C. MEHROTRA, *J. inorg. nuclear Chem.* **25**, 195 (1963); **25**, 201 (1963).

⁹) S. N. MISRA, T. N. MISRA and R. C. MEHROTRA, *J. Indian chem. Soc.* **43**, 61 (1966).

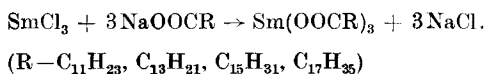
¹⁰) J. A. SEATON, F. G. SHERIFF and L. F. AUDREITH, *J. inorg. nuclear Chem.* **9**, 222 (1959).

only on prolonged refluxing with acetic anhydride with the dimeric bridged structure:

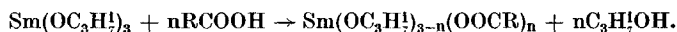


Oxoacetates of this type have been reported in the cases of titanium¹¹⁾ and zirconium¹²⁾. In view of the non-hydrolysable nature of lanthanon salts of the fatty acids⁸⁾⁹⁾ it was considered of interest to study the reaction of Samarium Chloride with acetic acid, acetic anhydride and their mixture. In all these cases quantitative yields of triacetate was obtained as final product. Measurements of molecular weight of these compounds in benzene showed them to be monomeric, in sharp contrast to the bridged structure suggested on the basis of their physicochemical properties.

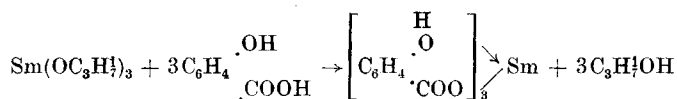
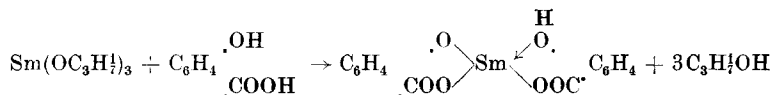
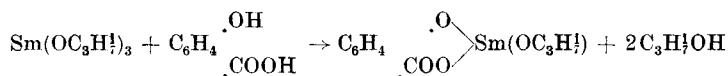
However, the higher acylates of samarium have been isolated from the double decomposition reaction:



The chloride acylates, however, could not be isolated from such reactions and hence the reactions of samarium isopropoxide with carboxylic acid (acetic, propionic, butyric, mandelic and salicylic) in different molar ratios have been carried out in benzene. The reactions of samarium isopropoxide with acetic, propionic and butyric can be represented by following equation: (where R = CH₃ or C₂H₅ or C₃H₇)



The reactions of samarium isopropoxide with salicylic acid can be typified by following equations:



¹¹⁾ K. C. PANDEY and R. C. MEHROTRA, Chem. Industry 1957, 114.

¹²⁾ R. N. KAPOOR and R. C. MEHROTRA, Chem. Industry 1958, 68; J. Amer. chem. Soc. 80, 3569 (1958).

However, the reaction with mandelic acid is parallel to the reaction with salicylic acid.

The technique of the reaction lies in adding required quantities of acid in benzene solution of samarium isopropoxide. Isopropanol was liberated, after refluxing the contents for four hours, was collected azeotropically with benzene. The product was obtained after distilling out excess solvent under reduced pressure and at the room temperature.

Experimental

Acids (palmitic, lauric, stearic and myristic) were purified after distilling under reduced pressure⁸⁾). Samarium was estimated as oxide. Samarium isopropoxide was prepared as described earlier¹³⁾.

The amount of higher fatty acid in cases of higher fatty acid derivatives was determined as described earlier.

Salicylate group was estimated by alkaline permanganate oxidation method¹⁴⁾.

Mandelate group was determined by method described by VERMA and PAUL¹⁵⁾.

Alkoxy contents in compounds were estimated by chromate oxidimetry¹⁶⁾.

Preparation of triacylates in aqueous medium

a) Preparation of Samarium trilaurate

The reaction involving aqueous solution of Samarium Chloride and Sodium Laurate solution led to the formation of precipitate which was filtered; washed thoroughly with

Table 1

Reactions of Samarium trichloride with sodium salts of fatty acids in aqueous medium

SmCl ₃ g.	Acid	Compound, state, yield (g) and m.pt.	Found Analysis		Calc.	
			Metal%	Acid%	Metal%	Acid%
6.20	Lauric	Sm(OOCC ₁₁ H ₂₃) ₃ white amorphous powder (11.98), 101–102 °C	19.82	80.07	21.10	79.90
5.30	Myristic	Sm(OOCC ₁₃ H ₂₇) ₃ white powder (13.2), 96–98 °C	17.62	80.22	18.06	81.94
5.60	Palmitic	Sm(OOCC ₁₅ H ₃₁) ₃ white amorphous powder (11.74), 89 °C	16.29	84.00	16.40	83.60
4.10	Stearic	Sm(OOCC ₁₇ H ₃₅) ₃ white amorphous powder (12.6), 83 °C	15.00	84.10	15.30	84.70

¹³⁾ B. S. SANKHLA, S. N. MISRA and R. N. KAPOOR, Chem. Industry 1965, 382.

¹⁴⁾ W. BATTGER, Newer Methods of volumetric chemical analysis, 1938 p. 61.

¹⁵⁾ M. R. VERMA and S. D. PAUL, J. Science Industry Research, 13 B, 347 (1954).

¹⁶⁾ D. C. BRADLEY, F. M. A. HALIM and W. WARDLAW, J. chem. Soc. [London] 1950, 3450.

Table 2
Reactions of Samarium isopropoxide with acetic, propionic and butyric acid in benzene

Alk-oxide in (g)	Acid (g)	Molar ratio	Compound, state, yield (g) and stoichiometry	Isopropanol in the azeotrope		% Found		Analysis			
				Found	Calculated	Metal	Isoprop-oxo	Metal	Acetoxy	% Calculated Isoprop-oxo	Acetoxy
Acetic acid											
1.10	0.21	1:1	$\text{Sm}(\text{OC}_2\text{H}_5)(\text{OOC}\cdot\text{CH}_3)$ light yellow solid, sparingly soluble in benzene (1.08)	0.21	0.22	45.3	36.0	17.9	45.9	36.1	18.0
1.63	0.61	1:2	$\text{Sm}(\text{OC}_2\text{H}_5)(\text{OOC}\cdot\text{CH}_3)_2$ light yellow crystalline solid sparingly soluble in benzene (1.61)	0.61	0.61	45.7	17.7	35.9	45.9	18.01	36.1
1.72	0.96	1:3	$\text{Sm}(\text{OOC}\cdot\text{CH}_3)_3$ light yellow solid, sparingly soluble in benzene (1.69)	0.95	0.96	45.9	—	54.4	45.9	—	54.1
Propionic acid											
1.184	0.265	1:1	$\text{Sm}(\text{OC}_2\text{H}_5)(\text{OOC}\cdot\text{C}_2\text{H}_5)$ yellowish crystalline solid, sparingly soluble in benzene (1.22)	0.22	0.217	43.2	34.2	21.2	44.0	34.7	21.3
1.344	0.607	1:2	$\text{Sm}(\text{OC}_2\text{H}_5)(\text{OOC}\cdot\text{C}_2\text{H}_5)_2$ yellowish crystalline solid, sparingly soluble in benzene (1.45)	0.48	0.49	41.8	16.1	41.0	42.4	16.6	41.0
1.076	0.7317	1:3	$\text{Sm}(\text{OOC}\cdot\text{C}_2\text{H}_5)_3$ yellowish crystalline solid sparingly soluble in benzene (1.20)	0.53	0.55	40.1	—	56.7	40.7	—	56.8

Table 3
Reactions of Samarium isopropoxide in the Salicylic acid mandelic acid

Alk-oxide in (g)	Acid (g)	Molar ratio	Compound, state, yield (g) and stoichiometry	Isopropanol in the azeotrope		Analysis						
				Found	Calculated	% Found	% Calculated	Metal	Acetoxy	Isoprop-oxo	Acetoxy	
Salicylic acid												
1.217	0.513	1:1	Sm(OC ₃ H ₇)(C ₇ H ₄ O ₃) yellowish white (1.23) insol in benzene	0.31	0.32	43.6	43.50	16.8	37.30	43.50	17.1	39.38
1.199	1.011	1:2	Sm(C ₇ H ₄ O ₃)(C ₇ H ₅ O ₃) yellowish white powder (1.51) insol in benzene	0.64	0.65	33.8	35.59	—	62.60	35.59	—	64.40
0.8801	1.113	1:3	Sm(C ₇ H ₄ O ₃)(C ₇ H ₃ O ₃)(C ₇ H ₆ O ₃) yellowish white powder (1.49) insol in benzene	0.46	0.47	26.0	26.92	—	74.10	26.92	—	73.10
Mandelic acid												
1.2057	0.5603	1:1	Sm(OC ₃ H ₇)(C ₈ H ₅ O ₃) yellowish white powder (1.20) insol in benzene	0.43	0.43	42.2	41.82	15.9	42.2	41.82	16.3	41.75
1.2150	1.1292	1:2	Sm(C ₈ H ₅ O ₃)(C ₈ H ₆ O ₃) yellowish white powder (1.60) insol in benzene	0.66	0.68	33.2	33.4	—	68.0	33.4	—	66.7
1.7628	2.4543	1:3	Sm(C ₈ H ₅ O ₃)(C ₈ H ₆ O ₃)(C ₈ H ₇ O ₃) yellowish white solid (3.23) insol in benzene	0.96	0.97	24.8	25.1	—	76.3	25.1	—	74.95

water finally with alcohol and dried in an oven at 110 °C. The product was crystallised anhydrous benzene.

Analysis: Found: Sm, 19.8, $C_{11}H_{23}COO$ 80.1. Calcd. for $Sm(OOC \cdot C_{11}H_{23})_3$: Sm 20.10, $C_{11}H_{23}COO$ 79.9%.

The reactions of sodium palmitate, sodium stearate and sodium myristate with samarium chloride are summarised in table 1.

b) The reactions of samarium isopropoxide with fatty acids

The reactions of samarium isopropoxide with acetic acid in molar ratio (1:1): Samarium isopropoxide (1.10 g), acetic acid (0.21 g) and benzene (78 g) were refluxed under a column for four hours. Isopropanol liberated was distilled out azeotropically with benzene. The product was obtained after distilling out the solvent under reduced pressure at the room temperature. (Yield, 1.10 g.)

Found: Sm 45.27, CH_3COO 17.96. Calc. for $Sm(OC_3H_7)_2(CH_3COO)$: Sm 45.94, CH_3COO 18.03%. Isopropanol found in the azeotrope 0.21 against 0.22 g. calculated for one mole.

For brevity the reactions of samarium isopropoxide with acetic, propionic and butyric acids in different molar ratios are summarised in table 2.

c) The reactions of samarium isopropoxide with α -hydroxy acids

The reactions of Samarium isopropoxide with mandelic acid in molar ratio 1:1. Samarium isopropoxide (1.206 g) was admitted to a solution of mandelic acid (0.560 g) in benzene (78 g) when an exothermic reaction was obtained. The reaction mixture was refluxed, isopropanol liberated was fractionated out azeotropically with benzene. The product was obtained after distilling out excess of the solvent. Under reduced pressure. (Yield, 1.20.)

Found: Sm 42.2, mandelate 42.2. Calcd. for $Sm(OC_3H_7)(O_3C_8H_5)$: Sm 41.82, mandelate 41.75%. Isopropanol found in the azeotrope, 0.431 g against 0.435 g calcd. for two moles.

The reaction of Samarium isopropoxide with salicylic and mandelic acid in different molar ratios are summarised in Table 3.

Authors thank Prof. R. C. KAPOOR, Head of the Department of Chemistry, University of Jodhpur, Jodhpur for providing laboratory facilities. One of us (M. HASAN) is thankful to C.S.I.R., New Delhi, for a research fellowship during the tenure of which this work was carried out.

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Bei der Redaktion eingegangen am 18. Dezember 1967.