

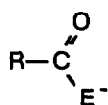
Crystalline Sodium Seleno- and Telluro-carboxylates:
Localization of Negative Charge on Electropositive Chalcogeno Atoms

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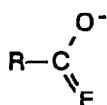
Summary: Crystalline sodium seleno- and telluro-carboxylates were prepared from the corresponding bis(acyl)selenide and tellurides with sodium ethoxide. The salts have the unsymmetrical ionic structure where the negative charge is localized on the selenium or tellurium atom.

The electronic structures of carboxylates and thiocarboxylates have been well-known to be resonance-hybrid of I and II.¹ However, preparation and structural study of alkali metal seleno- and telluro-carboxylates have remained unexplored due to their extreme instability towards oxygen. We report here the first synthesis and characterization of crystalline sodium seleno- and telluro-carboxylates and that they have the unsymmetrical ionic structures of III and IV where the negative charge is localized on electropositive chalcogeno atoms.

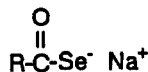


I

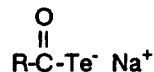
E=O, S



II

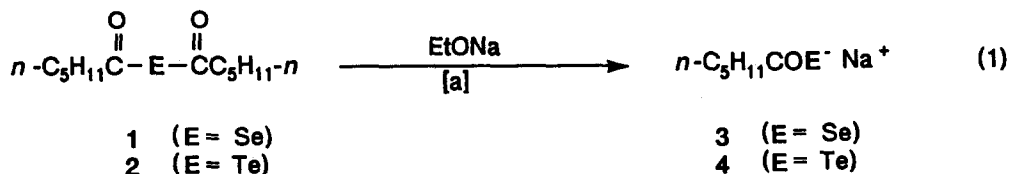


III



IV

The synthesis and isolation of crystalline sodium 1-pentanecarbo-selenoate (3) and -carbottelluroate (4) were achieved through treatment of the corresponding diacyl selenide (1) and telluride (2) with sodium ethoxide under an argon atmosphere, respectively (Eq. 1).² The salts (3) and (4) were stable under argon at 0 °C at least for one day without any appreciable decomposition, but they were highly sensitive towards oxygen.³ In Table 1 are listed the spectral data of 3 and 4. To our surprise, the carbonyl stretching frequencies of these salts appeared in the region of 1600 - 1620 cm⁻¹, close to those of chalcogeno esters (RCOER', E= S, Se, Te)⁴ (Figure 1).



[a] E = Se: Et₂O/hexane (1:1), -20 °C, 1 h; E = Te: THF, -20 °C, 2 h.

This shows that the carbon-oxygen bonds of the COSe and COTe groups in these salts have double bond character to the extent as the carbonyl groups in the chalcogeno esters and that the negative charge is localized on the chalcogeno atoms. The ⁷⁷Se nuclear magnetic resonance of 3 (in CD₃OD) appeared at δ 368.8 (from dimethyl selenide), while that of bis(1-pentane-carbonyl) diselenide (in CD₃OD) at δ 826.3.

The difference (δ = 457.5 ppm) between these chemical shifts is quite close to that (470 ppm) between diethyl diselenide and sodium ethaneselenolate whose negative charge is localized on the Se-atom (Table 2). In accord with the localization of negative charge on the Te atom in a sodium tellurocarboxylate, we have observed that the sodium salt reacts with a triorganosilyl chloride to form a Te-triorganosilyl tellurocarboxylate (5), in spite of strong affinity of a silyl group for an oxygen atom. The final product of this reaction is an O-triorganosilyl tellurocarboxylate (7) due to the facile rearrangement⁵ of 6 to 7 (Eq. 2). Thus, when *t*-butyldimethylchlorosilane was added to a solution of sodium 2-methylbenzenecarbotelluroate (5) in deuteriochloroform at -10 °C⁶, the color of the solution changed to yellow and then quickly to dark green.⁷ The reaction was monitored with ¹³C NMR spectroscopy. The band at δ 219.9 (¹³C=O) of the salt gradually decreased and two new bands appeared at δ

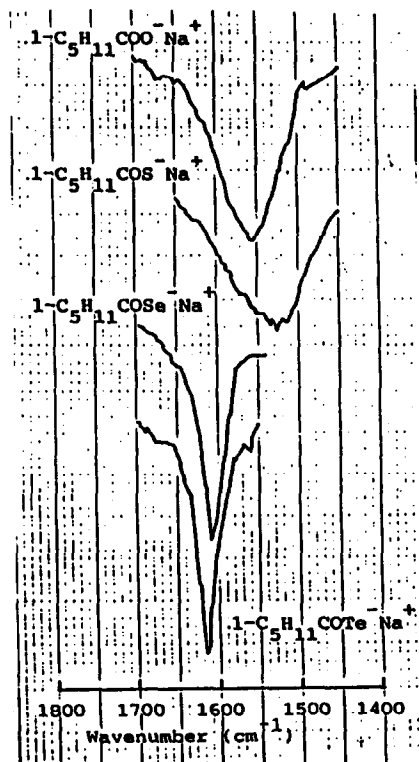


Figure 1. The $\nu\text{C}=\text{O}$ bands of sodium 1-hexanoate, 1-pentane-carbothioate, 1-pentane-carbo-selenoate (3), and 1-pentane-carbotelluroate (4) (Nujol).

be observed at δ 477.1 (CD₃OD) and δ 1759.1 (CDCl₃), respectively. In contrast to the sodium seleno- and telluro-carboxylates, alkali metal thiocarboxylates afford O-triorganosilyl thiocarboxylates **8** in good yields without formation of S-triorganosilyl esters **9** even as intermediates (Eq. 3).⁸ These results are consistent with the localization of the negative charge of seleno- or telluro-carboxylate on the selenium or tellurium atom. We suppose that the C=Se and C=Te are far less stable than the C=O double bond in seleno- and telluro-carboxylates and the negative charge of thiocarboxylate on both the oxygen and sulfur atoms implies that the C=S double bond structure is not very unfavorable in comparison to the structure of the C=O double bond.

References

- 1 RCO₂⁻: M. F. Dinville, C. Duval, and J. Cecomte, *Bull. Soc. Chim. Fr.*, **9**, 508 (1982); RCO₂⁻: V. V. Savant, J. Gopolakrishnam, and C. Patel, *Inorg. Chem.*, **9**, 748 (1970).
- 2 When bis(1-pentanecarbonyl) selenide (**1**) was treated with sodium ethoxide in pentane/ether at -20 °C, sodium 1-pentanecarboselenoate (**3**) was isolated in 85 % yield as colorless microfine crystals. Under the similar conditions sodium 1-pentanecarbotelluroate (**4**) was obtained in 82 % yield as orange microfine crystals.
- 3 For example, the salt (**3**) readily decomposed in air to give sodium 1-hexanoate together with red selenium. While, the telluroate (**4**) completely decomposed within a few minutes with liberation of black tellurium.
- 4 S. Kato, T. Murai, and M. Ishida, *Org. Prep. Proced. Int.*, **18**, 369 (1986).
- 5 The trimethylsilyl group of trimethylsilyl telluropivaloate migrates to the oxygen atom of the carbonyl group to give O-trimethylsilyl telluropivaloate; T. Severengiz and W. du Mont, *J. Chem. Soc., Chem. Commun.*, 1987, 820.
- 6 The reaction of sodium 2-methylbenzenecarbotelluroate with trimethylchlorosilane or of sodium benzenecarbotelluroate with t-butyldimethylchlorosilane proceeds too fast to detect the corresponding Te-triorganosilyl tellurocarboxylates by NMR spectroscopy.
- 7 In the case of the reaction of sodium benzenecarbotelluroate with trimethylchlorosilane, the color of the reaction mixture became finally to dark blue.
- 8 B. Martel and N. Duffaut, *C. R. Hebd. Seances Acad. Sci. Ser C*, **263**, 74 (1966); S. Kato, W. Akada, M. Mizuta, Y. Ishii, *Bull. Chem. Soc. Jpn.*, **46**, 244 (1973); M. Mikolajczyk, P. Kielbasinski, H. M. Schiebel, *J. Chem. Soc. Perkin Trans. I*, 1976, 564.