

Mössbauer and NMR study of novel Tin(IV)-lactames

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Abstract N-tributylstannylated 2-pyrrolidinone was reacted with tributyltin triflate in different molar ratios and the complex formation monitored using ^1H -NMR, ^{13}C -NMR and ^{119}Sn Mössbauer spectroscopy. Comparing the carbon NMR and tin Mössbauer results, a reaction scheme is suggested for the complexation which assumes the formation of a simultaneously O- and N-tributylstannylated pyrrolidinone cation. The formation of the only O-stannylated pyrrolidinone is also assumed to account for the non-constant Mössbauer parameters of the two tin environments in the distannylated pyrrolidinone cation when the ratio of tributyltin triflate is increased in the reaction.

Keywords Tin(IV) lactames · ^{119}Sn Mössbauer spectroscopy · NMR

1 Introduction

In a previous work we studied some cyclic N-trimethylsilylated carboxylic amide derivatives (ureas, lactames) [1] related to the recent interest in this field of coordination chemistry [2–4]. As an extension of that work here we have focused on tin as a heavier congener of silicon. N-tributylstannylated 2-pyrrolidinone was chosen as a model compound and its complexation with tributyltin triflate in different molar ratios was monitored.

The aim of this work was to prepare novel stannylated pyrrolidinone and characterize it by ^{119}Sn Mössbauer spectroscopy and NMR technique.

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2 Experimental

The model compound was prepared according to the common dehydration method starting from tributyltin oxide and pyrrolidinone [2]. After recrystallization from hexane, the pure substrate was dissolved in NMR-grade deuteriochloroform containing TMS (tetramethylsilane) as internal standard and mixed with stannyl triflate also dissolved in CDCl_3 , at triflate/substrate molar ratios of 0.3, 0.6, 1.2, 2.4 and 4.8. ^1H - and ^{13}C -NMR spectra of the solutions were taken at room temperature using Bruker Avance 250 MHz NMR spectrometer.

^{119}Sn Mössbauer spectra of frozen solution samples were recorded in transmission geometry with a conventional Mössbauer spectrometer (WISSEL) working in constant acceleration mode. The γ -rays were provided by a 10^9 Bq $^{119}\text{Sn}/\text{CaSnO}_3$ source. The measurements were performed at 78 K in a temperature-controlled through-flow type liquid nitrogen cryostat (Leybold). Isomer shifts are given relative to CaSnO_3 . The Mössbauer spectra were analyzed by least-square fitting of Lorentzian lines by the help of the MOSSWINN code [5].

3 Results and discussion

All peaks, even those derived from impurities (e.g. $(\text{Bu}_3\text{Sn})_2\text{O}$ and free pyrrolidinone with N-H group) present in the samples, could be assigned in the ^{13}C -NMR spectra. Furthermore, in the 'non-triflated' solution of the N-tributyltin pyrrolidinone, the coupling constant values of the $^1J_{\text{SnC}}$ and $^2J_{\text{SnCC}}$ were found to be 353.4 Hz (for ^{117}Sn) / 369.8 Hz (^{119}Sn) and 62.8 Hz (^{117}Sn) / 65.1 Hz (^{119}Sn), respectively.

Upon varying triflate/substrate molar ratios from 0.3, 0.6, 1.2, 2.4 to 4.8, the ^1H - and ^{13}C -NMR spectra exhibited a systematic and significant change of the chemical shifts (Fig. 1). The medium effect on the shift values could be neglected since solutions containing both the pyrrolidinone and triflate at different absolute concentrations but with identical molar ratio gave virtually the same spectra.

The well-separated shifts of the ring carbon atom directly attached to the nitrogen (near at 48 ppm) together with those of the carbonyl (~ 184 ppm, not shown) and the ring C atom next to the carbonyl (~ 31 ppm) and the Sn bonded α carbon (~ 13 ppm), all exhibit a saturation-type increase with increasing amount of triflate. However, butyl carbons at the β , γ (CH_2) and δ (CH_3) positions relative to the Sn atom, being rather insensitive to the nature of the tin-bounded ligand and to the chemical environment anyway, experience much less change in their shift values (near at 27, 28 and 14 ppm, respectively). In the region of the ring carbon shifts, new peaks are not observed, and this indicates a rapid equilibrium between the triflated and the non-triflated forms on the NMR time scale. In the butyl carbon region, the signals belonging to the hexabutyl distannoxane present as an impurity in some percents, tend to shift and grow into those of the tributyltin triflate, however, even at the molar ratio of 4.8 the ppm values markedly differ by a few tenths from those of the pure triflate. The chemically very sensitive Sn-C carbon peak characteristic to a more or less bound tributyltin triflate gives only a very weak signal at triflate to pyrrolidinone ratio 0.6.

On the basis of the NMR results, we can conclude that there is an equilibrium between the stannyl pyrrolidinone and the distannylated adduct, however, the

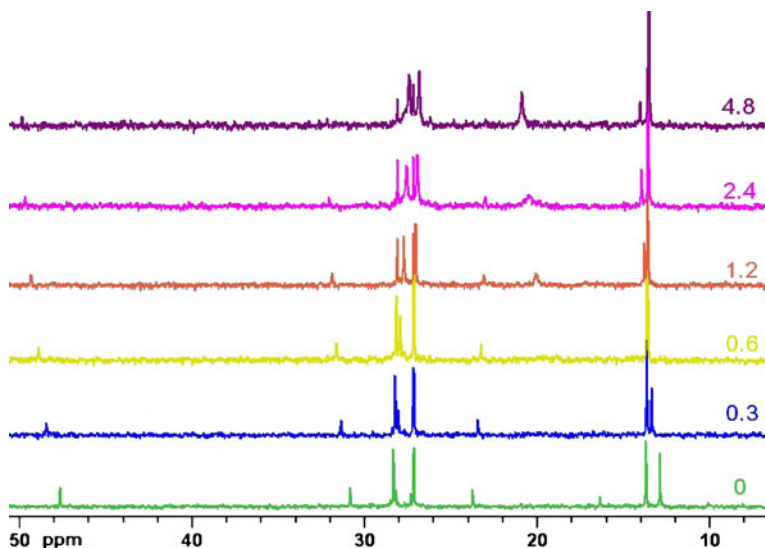


Fig. 1 A section of the ^{13}C NMR spectra for the tributylstannylated triflate-pyrrolidinone mixtures with different molar ratio of the triflate to pyrrolidinone indicated

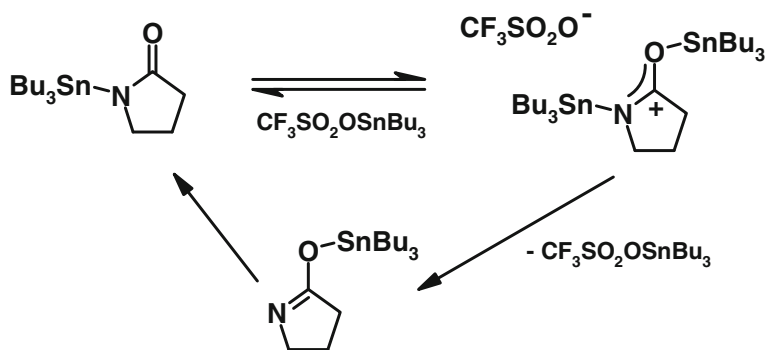
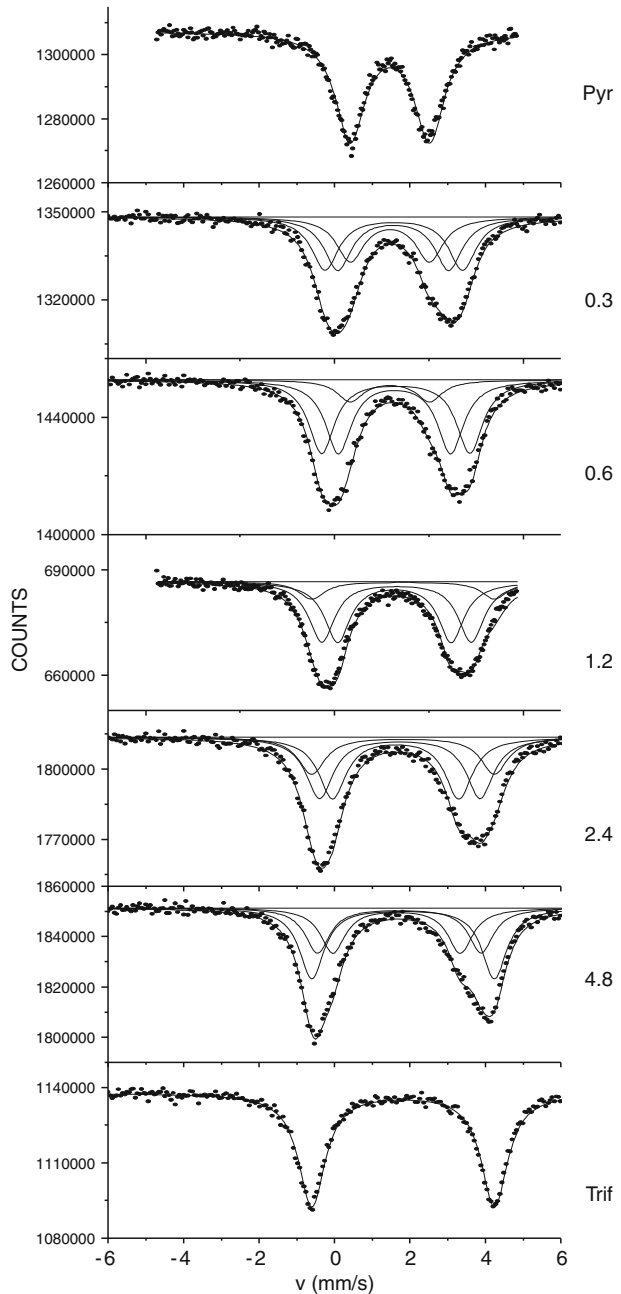


Fig. 2 A plausible mechanism of the reaction between N-tributyltin 2-pyrrolidinone and tributyltin triflate

equilibrium is pushed forward by an excess of triflate much higher than the stoichiometric amount (Fig. 2). On the NMR time scale the exchange rate of the tributylstannyl group is fast. A subordinate alternative decomposition route via the neutral O-stannylated pyrrolidinone isomer can not be completely excluded.

The ^{119}Sn Mössbauer spectra of tributyltin(IV) pyrrolidinone and tributyltin(IV) triflate and their mixture with different molar ratios are shown in Fig. 3. The Mössbauer spectra of tributyltin pyrrolidinone and that of stannyl triflate were decomposed into doublets with quadrupole splitting 2.10 mm/s and 4.84 mm/s, respectively, while all other spectra were evaluated as a superposition of 4 doublets. The isomer shift of all subspectra ($\delta = 1.36\text{--}1.71$ mm/s) reflects solely Sn^{IV} in these compounds. The relative occurrence of the components changes gradually with

Fig. 3 78 K ^{119}Sn Mössbauer spectra of N-tributyltin 2-pyrrolidinone (Pyr) and tributyltin triflate (Trif) and their solutions with molar ratios (Trif/Pyr) indicated



increasing molar ratio of the tributyltin triflate component in the solution, however, the relative spectral areas do not correspond well to the estimated equilibrium values taking into consideration usual relative f -factors for the components. Furthermore, the isomer shift and quadrupole splitting values of the doublets tentatively attributed

to the new Sn-microenvironments expected to form in the mixture varied gradually with increasing ratio of the tin triflate.

4 Conclusions

Comparing the carbon NMR and tin Mössbauer results, one can conclude that each of the two new doublets in the Mössbauer spectra represents the Mössbauer signal of tributylstannylated pyrrolidinone in the distannylated cationic form. One doublet is assigned to the O-stannyl moiety, the other one to the N-stannyl moiety.

Taking into consideration the Mössbauer spectra of tributylstannylated pyrrolidinone (N-stannylate) and tributyltin triflate (O-stannylate), the quadrupole doublet with lower quadrupole splitting ($\Delta = 2.94\text{--}3.38$ mm/s) can be tentatively assigned to the N-stannyl form and the other doublet ($\Delta = 3.65\text{--}4.34$ mm/s) to the O-stannyl form.

The shifting of the parameters of these doublets with increasing ratio of tributyltin triflate may be due to the presence of O-tributylstannylated pyrrolidinone (according to the mechanism shown in Fig. 2) which could not be resolved in the Mössbauer spectra and the amount of which obviously depends on the amount of tributyltin triflate.

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