Communications to the Editor

Evidence by ^{15}N CPMAS and $^{15}N-^{13}C$ REDOR NMR for Fixation of Atmospheric CO_2 by Amino Groups of Biopolymers in the Solid State

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Amino groups of organic and biological compounds can react with CO_2 in aqueous and nonaqueous environments to give the carbamates indicated in Figure 1.[1−4] The reaction is of importance in biological systems where it is used for the transport of CO_2.[3,4e,i,j] Mechanistic and pH-dependent studies indicate that ammonium groups have to be deprotonated before the reaction can occur. As HCO_3^- is preferentially formed at high pH,[4h] a maximum carbamate formation is observed at pH values corresponding to the pK_a values of the ammonium groups, i.e., for example 7 to 8 in the case of terminal amino groups of proteins,[4j] and pH 9 and 10 in the case of the α- and ϵ-amino groups of lysine.[4f]

However, to our knowledge, the reaction of amino groups of dry solids with atmospheric CO_2 under conditions of a reduced water content has not yet attracted attention. We have, therefore, studied this reaction using solid-state ^{15}N and ^{13}C NMR, in connection with cross-polarization (CP), magic angle spinning (MAS),[5] as well as $^{13}C-^{15}N$ REDOR (Rotational Echo Double Resonance) techniques.[6]

The compounds studied are α-ornithine-ω- ^{15}N-amino bola-amphiphile **1** and poly-l-lysine **2** (Figure 1). **1** was synthesized in a similar way as the lysine analogue.[7] The latter, **1**, forms spontaneously vesicular tubules by cooling micellar hot aqueous solutions at pH 10.5. Electron microscopy (Figure 1a) shows long tubules with monolayered membrane walls, where the amino headgroups are probably located inside the tubes and the polar tails outside (Figure 1a). The inner surface of the tubules is very large and thus favors solid-state reactions.

As the formation of tubular **1** strongly depends on pH, i.e., the state of deprotonation of the two amino and the carboxyl groups, we wanted to obtain more structural information concerning this problem using ^{15}N CPMAS spectroscopy.[9] Indeed, the spectrum of amorphous **1** lyophilized at pH 5 consists of a single line at about 5 ppm[10] (Figure 1b) which is typical for aliphatic $R-NH_3^+$ groups dissolved in water.[11] The sample did not show any alteration over a period of several weeks. By contrast, in the case of tubular **1** a shift to −13 ppm was observed (Figure 1c). This shift may be assigned either to a complete deprotonation of the ammonium group or to a water release and a partial deprotonation followed by the formation of ammonium−amino hydrogen bridges which could explain the stability of the tubular phase. Surprisingly, the spectrum of Figure 1c also contained a weak second signal at +47 ppm which grew slowly within several days during which the sample was kept in the rotor. When the sample was dissolved again in 2 M HCl and reprecipitated at pH 10.5 the low-field signal had disappeared but slowly reappeared.

We suspected carbon dioxide as the origin for these spectral changes and therefore exposed the sample of Figure 1c for 24 h to 1 atm of 90% enriched $^{13}CO_2$. As expected, the signal at +47 ppm strongly increased and the remaining amino headgroup signal shifted to −5 ppm (Figure 1d). The incorporation of $^{13}CO_2$ was followed by ^{13}C CPMAS NMR.[12] A few scans (Figure 1e) revealed a single dominant line at 164 ppm, which is typical for carbamates in aqueous solution.[13]

As the signal could stem from both the nonlabeled and the labeled amino groups of **1,** we also measured the $^{13}C-^{15}N$ dipolar coupling which yields directly the corresponding distance. In principle, this information could have been obtained by analysis of the static powder spectra,[15] but we preferred here to use the REDOR technique[6] that employs MAS and has the advantage of high chemical shift resolution and high sensitivity. The results are depicted in Figure 1f. In the REDOR spectrum the signal intensity of ^{13}C attached to ^{15}N is reduced as compared to the echo reference spectrum because of the dipolar $^{13}C-^{15}N$ coupling.[16] A reduction of ≈75% is observed indicating indeed the formation of $^{13}C-^{15}N$ pairs. Assuming that both amino groups react, the signal component arising from the $^{13}C-^{15}N$ pairs is therefore reduced to ≈50% of its original value. With the spinning

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(10) Reference: solid $^{15}NH_4Cl$. Some authors use neat nitromethane for ^{15}N CPMAS chemical shifts but although these shifts can be converted into solid $^{15}NH_4Cl$ reference by using δCH_3NO_2 + 338.1 ppm (355.3 ppm from CH_3NO_2 to saturated $^{15}NH_4Cl-D_2O$ and −17.2 ppm from saturated $^{15}NH_4Cl-D_2O$ to solid $^{15}NH_4Cl$),[15] they are not directly comparable because they have been calculated by using some approximate relationship between chemical shift references.

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