Isolation and Characterisation of a Carbamic Acid Complex

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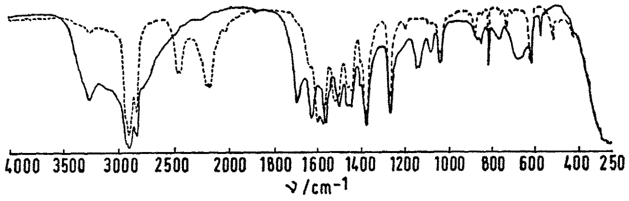
Summary Solid state i.r. examination of the amine–carbamic acid complex (**1**) suggests that a band below 1700 cm^{-1} may be useful in characterising such compounds.

CARBAMIC acids are notorious as fugitive species, often suspected but rarely characterised.[1,2] We report an unequivocal example with i.r. criteria which may prove useful elsewhere.

Addition of aqueous cyanamide to a saturated solution of carbon dioxide in aqueous dimethylamine at 80° led to a heavy crystalline precipitate which was filtered off and recrystallised from water. Microanalysis† agreed with the molecular formula $C_6H_{16}N_4O_2$, corresponding to 2 Me_2NH + $NH_2{\cdot}CN$ + CO_2; 1,1-dimethylguanidine was isolated as the picrate from an aqueous solution of the pure product. Its i.r. spectrum (Nujol: see Figure) revealed a complex situation in the 3200 cm^{-1} region together with three strong bands *ca.* 1600 cm^{-1} reminiscent of a primary enaminoketone[3] and unlike those of a guanidine or its salt.[4] We formulate the complex as (**1**), possibly with the unit structure shown, the bands at 1696, 1628, and 1564 cm^{-1} being attributed to $\nu(CO_2H)$, $\delta(NH_2)$, and conjugated $\nu(C{=}N)$[3b] respectively. Attempts to confirm this by deuteriation unexpectedly led to the salt (**2**), as shown by the much simplified $\nu(XD)$ pattern [two superimposed $\nu(ND_2)$], the absence of $\nu(CO_2D)$, and $\nu_{as}(CO_2^-)$ at 1600 cm^{-1}. We cannot explain this difference, which indeed is the reverse of what might have been expected.[5] Recrystallisation of (**2**) from water regenerated (**1**).



FIGURE

N.m.r. spectra (D_2O) were equivocal, indicating a mixture of species whose nature changed with time. Rapid potentiometric titration immediately following acidification of a

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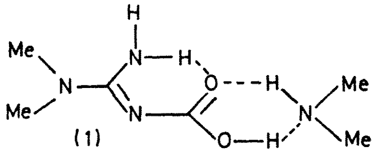
† Microanalyses were accurate and reproducible.

freshly made aqueous solution revealed two acidic species, pK_a 6·5 and 8·5, whose combined titre equalled the theoretical amount (0·42 and 0·63 equiv. respectively). Re-cycling slightly increased the former, which is plausibly due to carbon dioxide (lit.,[6] pK_a 6·4), and rapidly diminished the latter, which is therefore assigned to the carbamic acid. This remarkably high value presumably results from its unusually electron-rich environment, for by analogy amides are *ca.* 10^3 times more basic than urethanes.[7] The upper apparent pK_a (10·6), most readily interpreted as due to dimethylamine (lit.,[8] pK_a 10·73) with some contribution from the HCO_3^- ion (lit.,[6] pK_a 10·4), is also consistent with partial dissociation of (**1**) and, with the i.r. evidence, helps to eliminate the alternative structure (**3**) since 1,1-dimethylguanidine (lit.,[9] pK_a 13·4) is far too strong a base.



(1)

$Me_2N{\cdot}C(ND_2){=}N{\cdot}CO_2^-$ $Me_2ND_2^+$

(2)

$Me_2N{\cdot}CO_2H$ $Me_2N\ C(NH_2){=}NH$

(3)

We conclude that this is essentially a solid state phenomenon: dissociation in solution is extensive though reversible. For this reason potentiometric titration, though used here to some effect, may not always be helpful in characterisation. Microanalysis apart, i.r. spectroscopy is probably the method most generally applicable. The presence of a band at 1700—1650 cm^{-1}, unusually low for carboxylic acid carbonyl but too high for $\delta(NH_2)$, is particularly to be noted.

(*Received, May 3rd,* 1971; *Com.* 697.)

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