Stable Carbonium Ions. LIX.[1] Protonated Alkyl Carbamates and Their Cleavage to Protonated Carbamic Acids and Alkylcarbonium Ions

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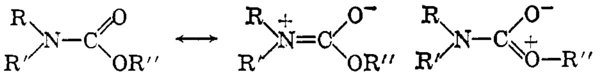
Abstract: Cleavage of alkyl carbamates in SO_2–SbF_5–FSO_3H solution leads to the formation of protonated carbamic acids and alkylcarbonium ions. Pmr parameters of protonated alkyl carbamates and carbamic acids have been measured at −60°. Carbonyl oxygen protonation was observed in all cases independently from N and O substituents.

We reported in earlier papers of this series that stereoisomers of protonated carboxylic acids[3a] and protonated esters[3b] can be studied by nmr. The stability of the stereoisomers is related to the bulkiness of the substituents of the α-carbon atom. Protonated carbamates and carbamic acids have not as yet been investigated by nmr. Studies of alkyl carbamates in oleum have shown that the acidolysis involves alkyl oxygen fission and not carbamyl oxygen fission.[4] Furthermore, the carbamic acids are unstable at higher temperatures (0–90°, depending on the N substituent) and lose carbon dioxide to give the corresponding amine identified as ammonium bisulfate. Prior to cleavage, depending on the concentration of the oleum, N-sulfonation can occur. As a result, a certain amount of sulfamic acid was formed in the acidolysis with 30 and 60% oleum.[4] Carbonium ions formed by alkyl oxygen cleavage have not been observed.[4]

A number of authors has found that carbamates, like amides, have a barrier to rotation around the C–N bond, and the magnitude of this barrier is related to the nature of N and O substituents.[5] Cross conjugation and double-bond character of the C–N bond as shown in II was described as an explanation of the hindered rotation. Hindered rotation around the C–O bond as in III was also observed by nmr.[6]

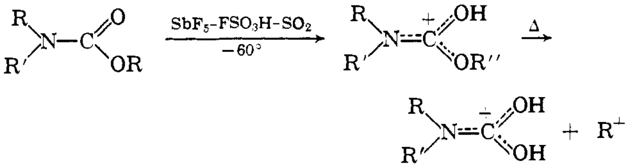


I II III

It was expected that investigation of protonated carbamates and carbamic acids would lead to a better understanding of their structure and the mechanism of their acidolysis.

Results and Discussion

Alkyl carbamates and carbamic acids give well-resolved nmr spectra in SbF_5–FSO_3H–SO_2 solution at −60°. Carbonyl oxygen protonation was observed in all cases. Independently of the nature of the substituents R, R′, and R″, the protonated carbamates, when raising the temperature, undergo alkyl oxygen cleavage to give the corresponding carbonium ion and protonated carbamic acid.



R, R′ = alkyl or hydrogen; R″ = alkyl

Protonated Carbamates. The proton on oxygen (1 H) of protonated ethyl carbamate (Figure 1) appears as a doublet centered at −9.86 ppm, caused by the coupling to the protons on nitrogen which appear as two broad singlets at −7.40 and −7.33 ppm. The ethyl hydrogens appear at −1.66 ppm as a triplet (3 H) and at −4.86 ppm as a quartet (2 H).

Protonated ethyl N-methylcarbamate (Figure 2) shows the proton on oxygen (1 H) at −9.71 ppm as the overlapping of a singlet with a doublet. It is expected that the proton on oxygen should show two resonance absorptions because of *cis* and *trans* isomers caused by hindered rotation around the C–O bond. If there is hindered rotation also around the C–O bond, a more complex pattern is expected. We observed for the proton on the carbonyl oxygen two resonances which seem to indicate that the C–N barrier to rotation is higher than that around the C–O bond. The doublet observed for one of the resonances is due to the splitting by the proton on nitrogen. The former (1 H) appears at −7.00 ppm as the overlapping of a quartet with a broad singlet. This is also due to *cis* and *trans* isomerism. For both forms the proton on nitrogen is expected to be coupled to the N-methyl hydrogens, but only one is coupled to the proton on oxygen. The N-methyl hydrogens (3 H) appear at −3.32 ppm as a pair of doublets corresponding to two different methyls equally coupled to the hydrogen on nitrogen. The absorption pattern of the ethyl group is also complicated by the existence of the two isomers. The methylene hydrogens (2 H) appear as two quartets centered at −4.76 ppm and the methyl hydrogens (3 H) as a triplet at −1.66 ppm.

The proton on oxygen (1 H) of protonated methyl

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[1] Part LVIII: G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **89**, 7072 (1967).

[2] National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

[3] (a) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **89**, 4752 (1967); (b) G. A. Olah, D. H. O'Brien, and A. M. White, *ibid.*, **89**, 5694 (1967).

[4] T. I. Bieber, *ibid.*, **75**, 1409 (1953).

[5] (a) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962); (b) E. Lustig, W. R. Benson, and N. Duy, *J. Org. Chem.*, **32**, 851 (1967); (c) T. M. Valega, *ibid.*, **31**, 1150 (1966); (d) E. H. White, M. C. Chen, and L. A. Dolak, *ibid.*, **31**, 3038 (1966).

[6] S. van der Werf, T. Olijusma, and J. B. F. N. Engberts, *Tetrahedron Letters*, **8**, 689 (1967).

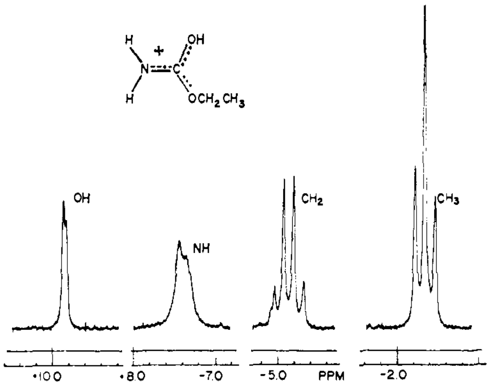


Figure 1.

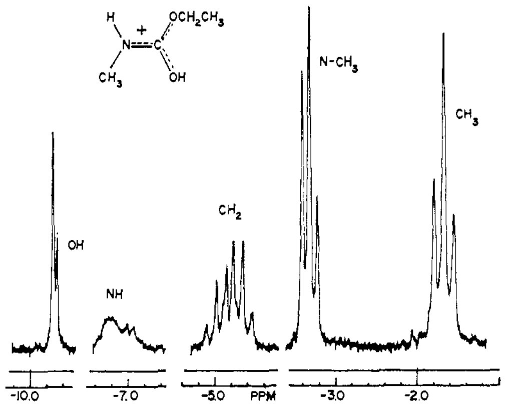


Figure 2.

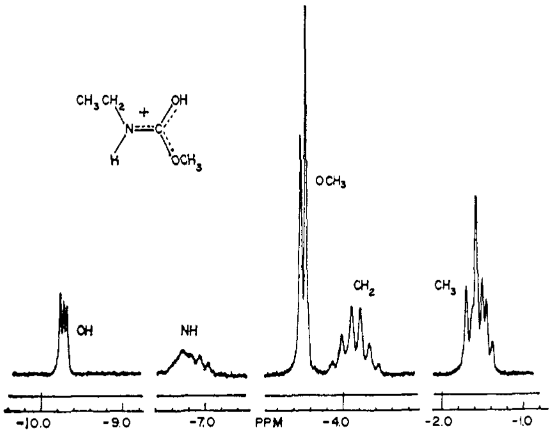


Figure 3.

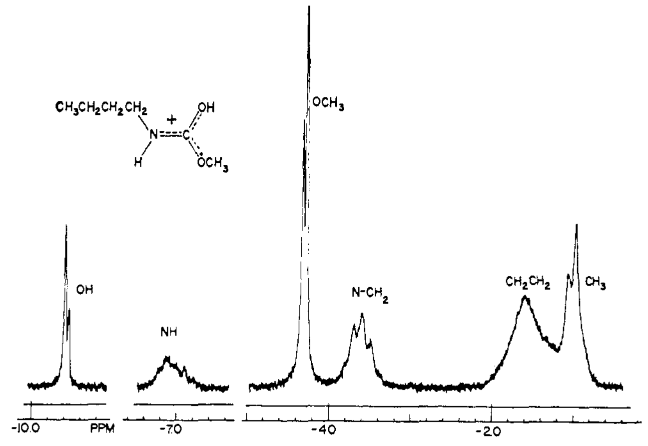


Figure 4.

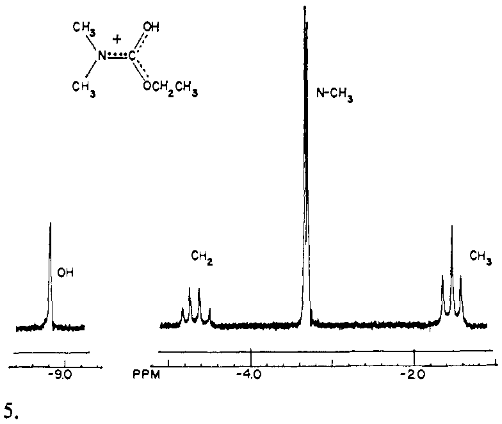


Figure 5.

N-ethylcarbamate (Figure 3) appears at -9.71 ppm as a singlet and at -9.65 ppm as a doublet. As in the case of ethyl N-methylcarbamate, the hindered rotation around the C–H bond introduces a chemical shift difference for the N substituents and C substituents. Only one of the isomers has the proton on oxygen coupled to the proton on nitrogen. The latter (1 H) appears at -7.18 ppm as a broad peak where two different NH are visible. The methyl hydrogens (3 H) are present in the spectrum at -4.38 and -4.43 ppm as two singlets of unequal intensities. The two singlets correspond to *cis* and *trans* isomers of the protonated species. The N-ethyl hydrogens appear at -3.75 ppm as two overlapping quartets (2 H) and at -1.45 ppm as two overlapping triplets (3 H).

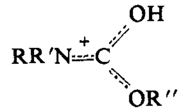
The nmr spectrum of protonated methyl N-*n*-butylcarbamate (Figure 4) shows the proton on oxygen (1 H) as the overlapping of a doublet with a singlet, centered at -9.57 ppm. The methyl protons (3 H) appear at -4.30 ppm as two singlets of unequal intensities. The population of *cis* and *trans* isomers seems to be unequal, and from the O-methyl and OH resonance it can be deduced that the *cis* isomer is favored. The N-alkyl hydrogens appear as unresolved multiplets with the α-methylene hydrogens coupled to the proton on nitrogen and the β-methylene hydrogens. The proton on nitrogen (1 H) appears at -7.10 ppm as a broad singlet.

The nmr spectrum of protonated ethyl N,N-dimethylcarbamate (Figure 5) shows the proton on oxygen (1 H) as a singlet at -9.18 ppm. Because of the similarity of the N substituents, the two isomers have identical chemical shifts for the proton on oxygen and the O-alkyl hydrogens. The N-methyl hydrogens (6 H) of the two isomers have different chemical shifts and appear at -3.31 and -3.46 ppm as two equal singlets.

Table I gives a summary of the pmr shifts and coupling constants of protonated alkyl carbamates.

Structure of Protonated Alkyl Carbamates. From the nmr spectra it can be deduced that protonation occurs only on the carbonyl oxygen atom. The partial double-bond character of the C–N bond gives rise to *cis* and *trans* isomers which can be identified for all protonated alkyl carbamates investigated. The down-

Table I. Pmr Chemical Shifts and Coupling Constants of Protonated Alkyl Carbamates in FSO_3H–SbF_5–SO_2 Solution at −60°[a]



R	R′	R′′	NR	NR′	OR′′	OH
H	H	C_2H_5	−7.35[b]	−7.40[b]	−1.66 −4.86 (−1.12) (−3.98)	−9.86[c]
CH_3	H	C_2H_5	−3.32[d] (−2.55)	−7.16[b] −6.98 (−5.60)	−1.66 −4.76 (−1.00) (−3.90)	−9.71 −9.66[e]
C_2H_5	H	CH_3	−1.45 −3.75 (−1.00) (−3.10)	−7.18 (−6.05)	−4.38 −4.43 (−3.53) (−3.56)	−9.71 −9.68[f]
n-C_4H_9	H	CH_3	−1.00 −1.56 −3.60 (−0.76) (−1.30) (−3.00)	−7.10[b] (−5.68)	−4.30 (−3.50)	−9.58 −9.55[g]
CH_3	CH_3	C_2H_5	−3.31 (−2.80)	−3.46 (−2.80)	−1.55 −4.80 (−1.06) (−3.93)	−9.18

[a] In parentheses are the chemical shifts of the corresponding alkyl carbamates in SO_2 at −60°. [b] Broad singlet. [c] Doublet, J_{OH-NH} = 1.9 Hz. [d] Two averaging doublets, J_{CH_3-NH} = 5.0 Hz. [e] Doublet, J_{OH-NH} = 2.8 Hz. [f] Doublet, J_{OH-NH} = 2.8 Hz. [g] Doublet, J_{OH-NH} = 2.8 Hz.

field shifts caused by protonation indicate that for N,N-substituted carbamates the positive charge is located mostly on nitrogen; *i.e.*, protonated ethyl N,N-dimethylcarbamate shows a downfield shift of 1.60 ppm for the N-methyl and only 0.87 ppm for the methylene hydrogens. The shifts of the N and O substituents are equal for protonated N-monosubstituted carbamates which would indicate equal distribution of the positive charge. The proton on oxygen in protonated N-monosubstituted carbamates appears as two peaks corresponding to *cis* and *trans* isomers. Only one of the isomers shows a coupling of this proton to the proton on nitrogen.

Cleavage of Protonated Carbamates. Even at low temperature (−60°) protonated alkyl carbamates undergo alkyl oxygen cleavage to give carbonium ions and protonated carbamic acids. The rate of cleavage depends on the nature of the N substituents, but mostly of the O substituents. Qualitatively it was observed that secondary alkyl carbamates are cleaved very rapidly. Cleavage of primary alkyl carbamates is somewhat slower and is slowest for methyl carbamates. The formed alkylcarbonium ions are directly observed only if their stability is sufficient under the reaction conditions. Unstable species such as secondary and primary carbonium ions undergo rearrangement to tertiary cations. Methyl and ethyl cations were not observed in any case although their existence as intermediates is proven by the structure of by-products. Methyl and ethyl cations react with the solvent in different ways. Ethyl fluoride was formed *via* abstraction of fluoride ion from the solvent in quantitative yield in the acidolysis of ethyl carbamates. The stability of alkylcarbonium ions and their structure under the same conditions has been thoroughly investigated previously[7] and will not be further discussed here. It was also found that alkyl oxygen cleavage which occurs in the case of some protonated primary carboxylic acid esters leads to the same type of by-products.[3b]

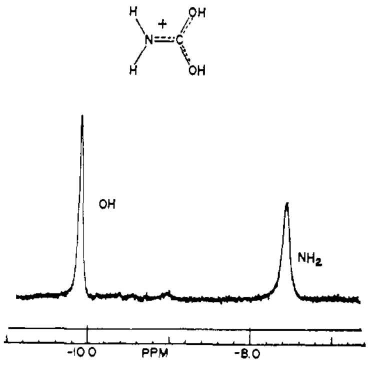


Figure 6.

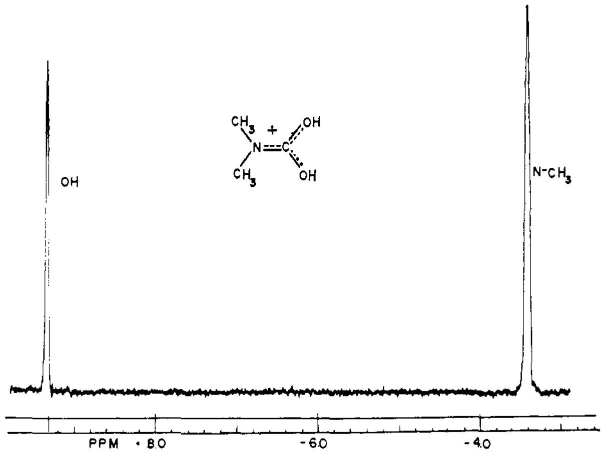


Figure 7.

Protonated Carbamic Acids. The carbamic acids, formed by the alkyl oxygen cleavage of their esters, are protonated in the strong acid system used and no loss of carbon dioxide was observed. At −60° the nmr spectra of the protonated carbamic acids were well resolved and show exclusively carbonyl oxygen protonation. The rate of proton exchange is higher for carbamic acids than for their esters, and a fine structure of the OH resonance is more difficult to identify.

It is remarkable that protonation of carbamic acid itself (Figure 6) occurs also only on the carbonyl oxygen atom. The two OH groups give rise to a singlet at −10.10 ppm. The NH hydrogens (2 H) appear at −7.45 ppm as a broad singlet.

The nmr spectrum of protonated N,N-dimethylcarbamic acid (Figure 7) shows one singlet at −3.38 ppm for the methyl hydrogens (6 H) and one singlet at −9.30 ppm for the proton on oxygen (2 H). A similar spectrum is observed for protonated N,N-diethylcarbamic acid. The OH resonance appears at −9.20 ppm as a sharp singlet (2 H). Protonated N-methylcarbamic acid (Figure 8) has a more complicated nmr spectrum, showing the methyl hydrogens at −3.36 ppm as a doublet caused by the coupling to the proton on

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(7) G. O. Olah and J. Lukas, *J. Am. Chem. Soc.*, **89**, 4739 (1967).

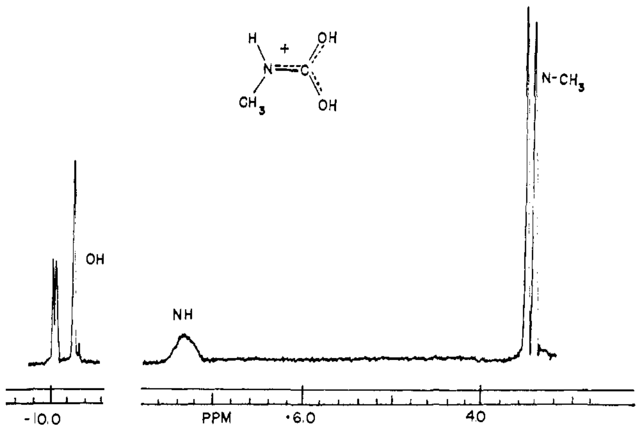


Figure 8.

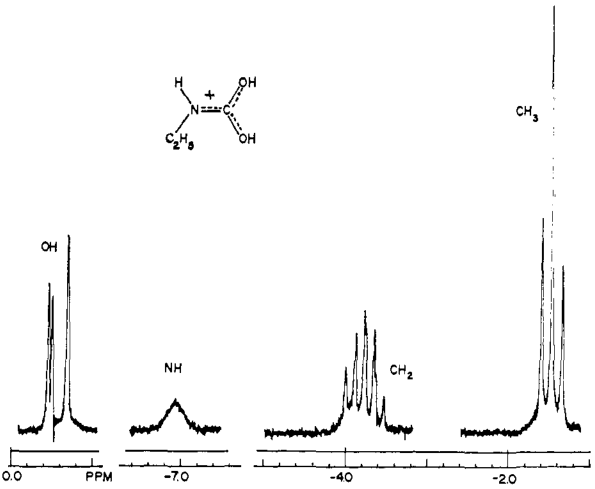
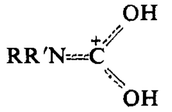


Figure 9.

nitrogen. The two OH groups appear as two resonances, at −9.91 and −9.72 ppm. The low-field peak is a doublet caused by the coupling to the proton on nitrogen. The latter appears at −7.23 ppm as a broad singlet (1 H). The spectrum of protonated N-ethylcarbamic acid (Figure 9) shows analogous features. There are two resonances for the protons on oxygen (2 H), at 9.61 and −9.60 ppm, the low-field peak being a doublet. The ethyl hydrogens appear as a triplet (3 H) at −1.46 ppm and two quartets (2 H) at −3.76 ppm. The methylene hydrogens are coupled to the proton on nitrogen.

Table II gives a summary of protonated pmr chemical shifts and coupling constants of protonated carbamic acids.

Table II. Pmr Chemical Shifts and Coupling Constants of Protonated Carbamic Acids in FSO_3H–SbF_5–SO_2 Solution at −60°

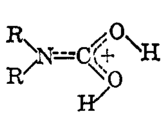


$RR'N{=}C^{+}(OH)_2$

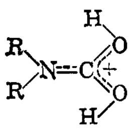
R	R′	NR	NR′	OH
H	H	−7.45[a]	−7.45[a]	−10.10[a]
CH_3	H	−3.36[b]	−7.23	−9.91[c] −9.72
C_2H_5	H	−1.46 −3.76	−7.20	−9.81[d] −9.60
CH_3	CH_3	−3.38	−3.38	−9.30

[a] Broad singlet. [b] Doublet, J_{CH_3-NH} = 5.0 Hz. [c] Doublet, J_{OH-NH} = 2.8 Hz. [d] Doublet, J_{OH-NH} = 2.8 Hz.

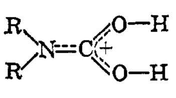
Structure of Protonated Carbamic Acids. The protonated N,N-disubstituted carbamic acids show only one resonance for the protons on oxygen indicating relatively free rotation about the C–O bond, and no isomers can be identified. The existence of the protonated species in a rigid conformation with magnetically equivalent hydroxylic protons as in IV, V, and VI is less probable.



IV



V



VI

Protonated N-alkylcarbamic acids have a similar structure. The two resonances due to the hydroxylic protons correspond to two different OH protons, but this difference is due to the hindered rotation about the C–N bond. It is noteworthy that only one of the OH protons is coupled to the proton on nitrogen. It can be said that this coupling is an allylic-type coupling where two carbon atoms are replaced by heteroatoms, oxygen and nitrogen. As was shown previously for similar cases,[8] the principles governing allylic couplings can also be applied to heteroatom systems. The resonance corresponding to the *cis* isomer would appear as a doublet and that corresponding to the *trans* isomer, as a singlet. This would not account for a C–O hindered rotation; thus isomers as depicted as IV, V, and VI were not identified.

Protonated carbamic acids are effective carbamylating agents. Our studies in this respect will be published separately.

Experimental Section

Materials. Alkyl carbamates were reagent grade and used without further purification. The N-monosubstituted and N,N-disubstituted carbamates have been prepared from the corresponding alkyl isocyanate and N,N-dialkylcarbamoyl chlorides. The isocyanate or carbamoyl chloride reacts with the alcohol in the presence of pyridine in chloroform solution to give the corresponding carbamates. The distilled products have been identified by their ir and nmr spectra and had the reported physical properties. The substituted carbamic acids have been prepared *in situ* from the carbamic acid esters by warming the acid solutions to between −20 and −40°. The spectra of protonated carbamic acids obtained from different esters had identical nmr patterns.

Nmr Spectra. Varian Associates Model A-56/60 A and HA 60-IL nmr spectrometers with variable-temperature probes were used for all spectra. The coupling constants are accurate to within 0.1 Hz.

Preparation of Protonated Alkyl Carbamates and Their Cleavage to Protonated Carbamic Acids and Alkylcarbonium Ions. Samples of protonated alkyl carbamates were prepared by dissolving 1.5 ml of SbF_5–FSO_3H (1:1 *M* solution) in an equal volume of sulfur dioxide and cooling it to −78°. The ester (0.3 g) was dissolved in 2 ml of sulfur dioxide, cooled to −78°, and added to the acid solution. The protonated carbamic acids and alkylcarbonium ions have been obtained by warming the ester solution prepared as above until cleavage was completed. The solvent acid peaks (SbF_5–FSO_3H) and those of the cleaved carbonium ions and their derived products (alkyl fluorides) have been deleted from the spectra for simplicity.

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(8) G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **90**, 405 (1968).