

# Generation of Carbamic Acid (NH<sub>2</sub>CO<sub>2</sub>H) and its Radical Cation as Stable Species in the Gas Phase\*\*

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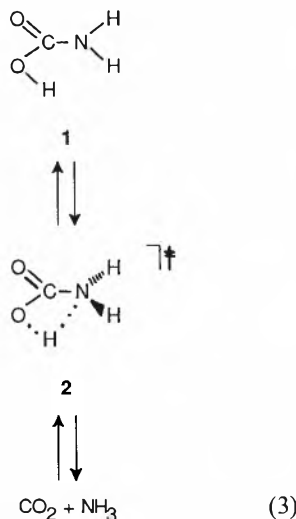
**Abstract:** Thermolysis of ammonium carbamate yields the hitherto unknown free carbamic acid (H<sub>2</sub>N-CO-OH), which is characterized by means of mass spectrometric methods. In the gas phase high energy barriers prevent the spontaneous dissociation of both neutral carbamic acid (1) and its radical cation (1<sup>⊕</sup>).

Statements of the kind that «carbonic acid, (HO)<sub>2</sub>CO, and its monoamide, i.e. carbamic acid H<sub>2</sub>NCOOH, cannot exist in the free state»<sup>[1,2]</sup> are warranted insofar as it has not been possible to prepare these species in solution. This is because in solution acid/base as well as solvent catalysis promotes a rapid decomposition and, in case of (HO)<sub>2</sub>CO, also the deprotonation into the hydrogencarbonate ion<sup>[2,3]</sup>:



In the gas phase, however, quite a different situation obtains; the (exothermic) unimolecular dissociation of H<sub>2</sub>CO<sub>3</sub> is predicted by ab initio MO studies<sup>[4]</sup> to be hampered by a significant energy barrier (> 40 kcal/mol) and thus, the free carbonic acid,

(HO)<sub>2</sub>CO, should exist as a stable molecule. Indeed, recent experiments<sup>[5]</sup> clearly demonstrate that thermolysis of NH<sub>4</sub>HCO<sub>3</sub> not only yields NH<sub>3</sub>, CO<sub>2</sub>, and H<sub>2</sub>O but also the long-sought H<sub>2</sub>CO<sub>3</sub>, which, together with its radical cation could be identified as stable species by using mass spectrometric techniques. Encouraged by this result and the ab initio prediction<sup>[6]</sup> that reaction (3) should also have a sizeable barrier (59.5 kcal/mol at the a sizeable barrier (59.5 kcal/mol at the 3-21G//3-21G level of theory), we set out to generate the hitherto unknown carbamic acid (1).



We report here that the free carbamic acid 1 and its radical cation 1<sup>⊕</sup> can easily be generated as stable species in the gas phase by thermolysis experiments on am-

monium carbamate, NH<sub>4</sub>CO<sub>2</sub>NH<sub>2</sub>, analogous to our experiments on NH<sub>4</sub>HCO<sub>3</sub> for the production of H<sub>2</sub>CO<sub>3</sub><sup>[5]</sup>.

To this end finely powdered ammonium carbamate was introduced in the ion source of a VG analytical ZAB-2F mass spectrometer by the standard direct insertion probe and heated by the heat transfer of the ion source block (*T* = 150 °C) to the quartz sample holder. Ionization of the neutrals formed was brought about by 70 eV electrons (emission current 50 μA). The mass spectrum obtained showed signals at *m/z* 17 (NH<sub>3</sub><sup>⊕</sup>), *m/z* 18 (H<sub>2</sub>O<sup>⊕</sup>, NH<sub>4</sub><sup>⊕</sup>), *m/z* 44 (CO<sub>2</sub><sup>⊕</sup>), and also *m/z* 61. The *m/z* 61 peak was 1–5% of the base peak (*m/z* 44), but irregular evaporation caused extremely strong intensity fluctuations.

An exact mass measurement was performed on the *m/z* 61 ions and the result, 61.01604 dalton, is only compatible with the elemental composition CH<sub>3</sub>NO<sub>2</sub> (calculated 61.01637 dalton); the next best combination, C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>, has a calculated mass of 61.02895 dalton, so no ambiguity as to the elemental composition exists. Replacement of the hydrogen atoms by deuterium (i.e. thermolysis of ND<sub>4</sub>CO<sub>2</sub>ND<sub>2</sub>, synthesized from ND<sub>3</sub> and CO<sub>2</sub>) resulted in a mass shift *m/z* 61 → *m/z* 64. For the undeuterated compound no signal was present at *m/z* 78, and a metastable transition for the reaction *m/z* 78 → *m/z* 61 + NH<sub>3</sub> could not be detected. Lowering the temperature used to thermolyze the sample resulted in the disappearance of the *m/z* 61 ions. These findings strongly suggest that the CH<sub>3</sub>NO<sub>2</sub><sup>⊕</sup> ions have been generated by direct ionization of the corresponding neutral molecule and not as fragment ions produced by loss of NH<sub>3</sub> from ionized ammonium carbamate.

Collision-induced decomposition of the mass selected *m/z* 61 and *m/z* 64 ions (MS/MS experiments<sup>[7]</sup>) yields the collisional activation<sup>[8]</sup> (CA) spectra shown in Fig. 1 (a and b). Comparison of the two spectra indicates that *m/z* 17 in Fig. 1a is mainly NH<sub>3</sub><sup>⊕</sup> (and not OH<sup>⊕</sup>) and that *m/z* 44 largely consists of H<sub>2</sub>H-C=O<sup>⊕</sup>. What is more important, all abundant fragment ions are compatible with our proposal that the *m/z* 61 ions have the structure of ionized carbamic acid 1<sup>⊕</sup> (Scheme 1). In particular, we note, that the isomeric form HN=C(OH)<sub>2</sub><sup>⊕</sup> is expected to decompose via different fragmentation routes (intense loss of H<sub>2</sub>O). Therefore, this species is not any longer considered as a possible candidate for the thermolysis product.

Encouraged by our recent neutralization-reionization (NRMS<sup>[9]</sup>) experiments which made it possible to generate exotic molecules like HC≡COH<sup>[10a]</sup>, HC≡CNH<sub>2</sub><sup>[10b]</sup>, and XC≡CY with X, Y = OH, NH<sub>2</sub><sup>[10c]</sup> by neutralizing the corresponding radical cations in the gas phase, we have also performed such an experiment with 1<sup>⊕</sup> and its D<sub>3</sub>-labeled analogue. The NRMS spectra (Fig. 1c, d) leave no doubt that a significant fraction of

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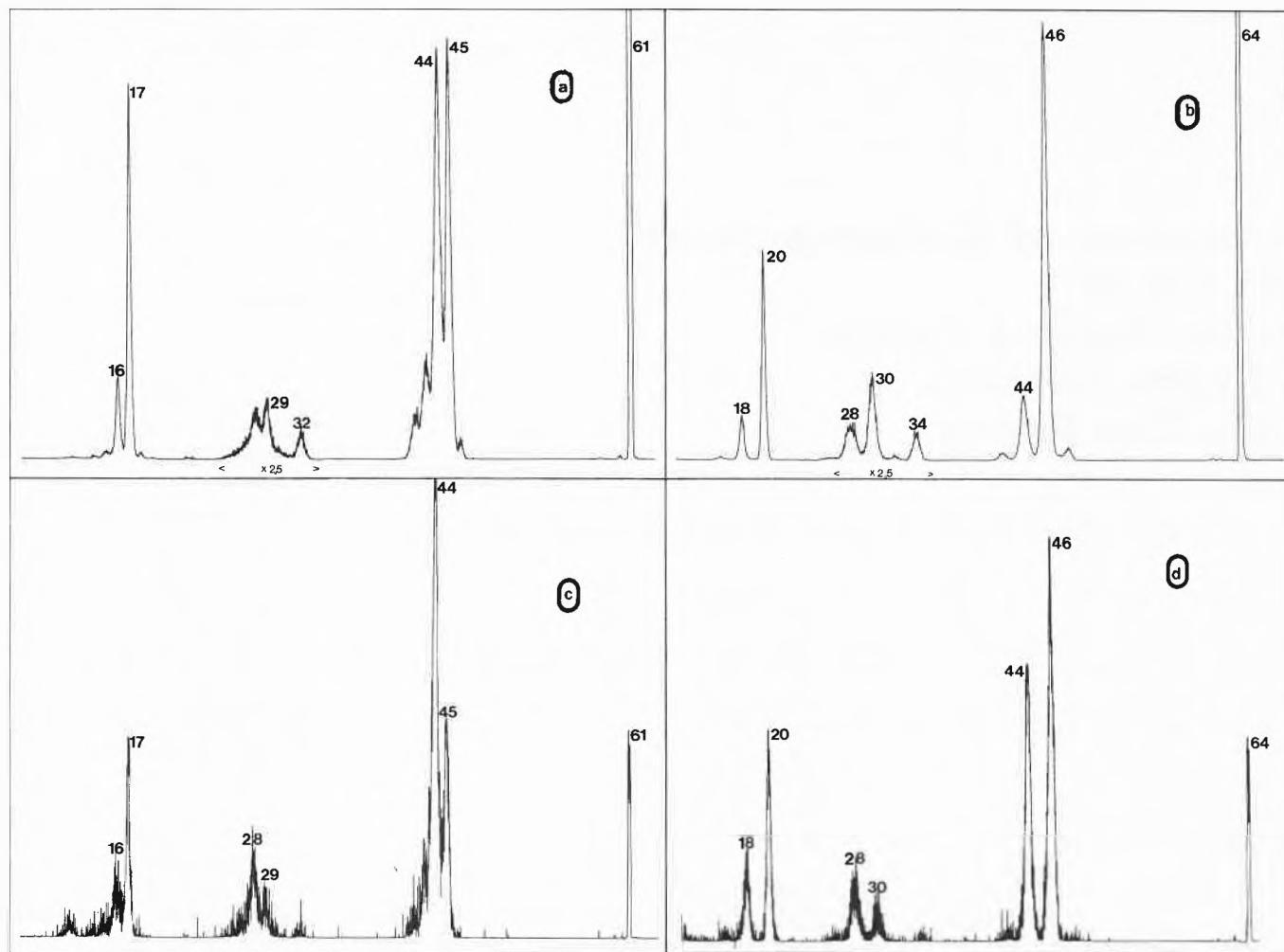


Fig. 1. (a) and (b): CA mass spectra of  $m/z$  61 ( $\text{NH}_2\text{CO}_2\text{H}^{\oplus}$ ) and  $m/z$  64 ( $\text{ND}_2\text{CO}_2\text{D}^{\oplus}$ ), respectively; (c) and (d): NRMS spectra of  $m/z$  61 ( $\text{NH}_2\text{CO}_2\text{H}^{\oplus}$ ) and  $m/z$  64 ( $\text{ND}_2\text{CO}_2\text{D}^{\oplus}$ ), respectively, using xenon for neutralization and oxygen for re-ionization.

Scheme 1

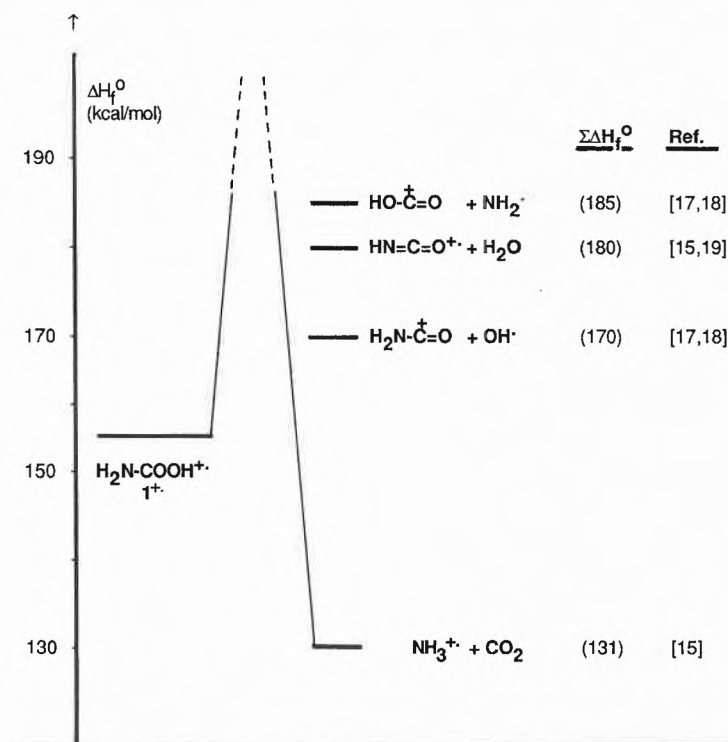
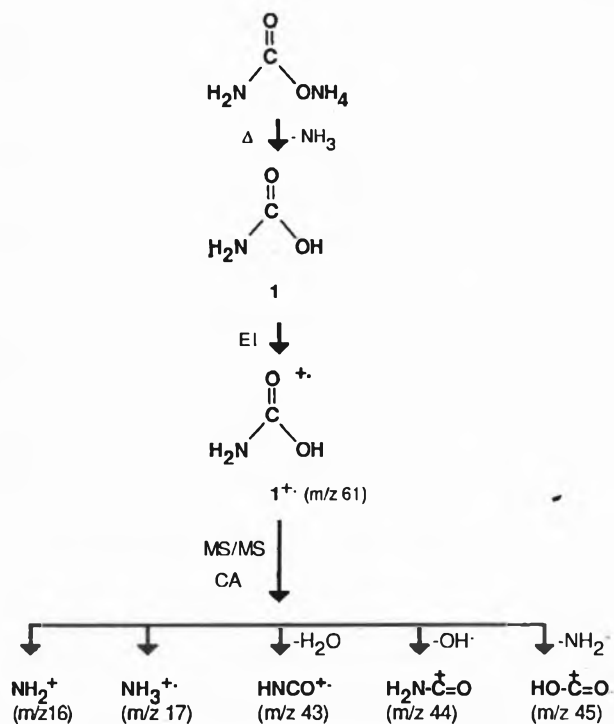


Fig. 2. Enthalpies of reaction for the major dissociation processes of  $1^{\oplus}$  (data are given in kcal/mol and taken from the references indicated).

the  $m/z$  61 and  $m/z$  64 ions remain intact upon neutralization followed by reionization. Note that the peak intensities of the  $m/z$  43–46 clusters in the two NRMS spectra are consistent with the assumption that about 70% of the  $m/z$  44 peak in the spectrum of the unlabeled ions is due to  $\text{CO}_2^{\oplus\ominus}$  generated by the reionization of  $\text{CO}_2$  formed in the dissociation of the neutral acid into  $\text{CO}_2$  and  $\text{NH}_3$ . Thus, we conclude that both **1** and  $\mathbf{1}^{\oplus\ominus}$  are stable species in the gas phase. For neutral carbamic acid we have already mentioned that its decomposition is prevented by a high energy barrier (reaction (3)). Using the same level of theory (3-21G//3-21G) ab initio MO calculations indicate that the critical energy for the analogous dissociation of  $\mathbf{1}^{\oplus\ominus}$  into  $\text{NH}_3^{\oplus\ominus}$  and  $\text{CO}_2$  requires as much as 71.6 kcal/mol<sup>[11]</sup>. This large barrier<sup>[12]</sup> for an otherwise exothermic reaction (see below) together with the estimate that all remaining processes of  $\mathbf{1}^{\oplus\ominus}$  are highly endothermic (see below) explain the observation of ions  $\mathbf{1}^{\oplus\ominus}$  as stable species in the gas phase.

#### Thermochemistry of **1** and $\mathbf{1}^{\oplus\ominus}$

A MNDO calculation of the heat of formation,  $\Delta H_f^0$ , of the neutral molecule yielded  $\Delta H_f^0(\mathbf{1}) = -96$  kcal/mol. This value is in fair agreement with that obtained on the basis of Benson's additivity rules<sup>[13]</sup> and the reported  $\Delta H_f^0$  value of  $\text{H}_2\text{NC}(\text{O})\text{OC}_3\text{H}_7$  ( $-112.7$  kcal/mol<sup>[14]</sup>),  $\Delta H_f^0(\mathbf{1}) = -104$  kcal/mol<sup>[14]</sup>. Considering that  $\Sigma\Delta H_f^0(\text{NH}_3) + \Delta H_f^0(\text{CO}_2) = -105$  kcal/mol<sup>[14]</sup> it follows that the dissociation of **1** in the gas phase is either thermoneutral or (slightly) exothermic.

For the radical cation  $\mathbf{1}^{\oplus\ominus}$  the MNDO method yielded  $\Delta H_f^0(\mathbf{1}^{\oplus\ominus}) = 150$  kcal/mol, a value close to that, 156 kcal/mol, ob-

tained on the basis of  $\Delta H_f^0(\mathbf{1}^{\oplus\ominus}) = \Delta H_f^0(\mathbf{1}) + IE(\mathbf{1})$ <sup>[16]</sup>. This value was used to construct the energy diagram shown in Fig. 2. It is seen that all dissociation reactions are strongly endothermic with the exception of the process  $\mathbf{1}^{\oplus\ominus} \rightarrow \text{NH}_3^{\oplus} + \text{CO}_2$  which however has a high activation barrier. Thus it is not surprising that the carbamic acid radical cation is observed as a stable species.

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