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Ion/molecule reactions of protonated diglycine: an electrospray ionization flow tube reactor experiment

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Abstract

Reactions of protonated diglycine, GLY_2H^+, with methanol, ammonia, and a series of methylamines were studied under thermal conditions with a combination of an electrospray ion source and a flow tube reactor. The major primary reaction product in all of the systems studied is the complex formed between the ionic and neutral reagents in a ternary association reaction involving the helium carrier gas and oxygen or nitrogen molecules as collisionally stabilizing species. Effective binary rate constants were determined experimentally and compared with calculated ion dipole collision rate constants. Proton transfer was observed from GLY_2H^+ to trimethylamine but not to any of the other reagents studied. Secondary products observed include formation of protonated mixed trimers of GLY_2 with two amine molecules. In the case of methanol, a secondary product is the protonated mixed dimer of GLY_2 and dimethylether. The results will be discussed in the light of the mechanisms of hydrogen-deuterium (H-D) exchange of GLY_2H^+ with deuterated isotopomers of methanol and ammonia studied previously by various groups. (Int J Mass Spectrom 179/180 (1998) 165–171) © 1998 Elsevier Science B.V.

Keywords: Peptides; ESI; Sift; Ion complexes; H-D exchange

1. Introduction

There has been considerable interest in recent years in the analytical capabilities of mass spectrometry in the field of biomolecules and in the possibility of studying conformations of proteins by gas phase ion chemistry. As part of that effort, techniques have been developed for studying hydrogen-deuterium (H-D) exchange between protonated peptides and deuterated solvent molecules such as ND_3, D_2O, and CH_3OD [1–7]. The proposed H-D exchange mechanism invokes formation of an intermediate complex with multiple hydrogen bonding. Most of the work has been carried out under the very high vacuum conditions of Fourier transform ion cyclotron resonance (FTICR) ion sources and the complexes have not been observed directly. We have studied in recent years insertion reactions of ammonia and methanol into proton bound dimers [8,9] and into protonated crown ethers [10,11] with special emphasis on the effect of multiple hydrogen bonding on reactivity. The insertion complexes were observed experimentally in a selected ion flow tube (SIFT) at pressures of

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Dedicated to Professor Fulvio Cacace in recognition of his outstanding contributions for many decades to gas-phase ion chemistry and physics.

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a few tenths of a Torr. Ammonia and methanol are precisely the H-D exchange reagents employed for the peptides and invoked in formation of the complexes, with ND_3 being the most effective reagent for facile exchange of labile hydrogens in protonated peptides [2,4–7]. The present article addresses the formation of reaction complexes between protonated diglycine, GLY_2H^+, with ammonia, methanol, and a series of amines.

The study of ion/molecule reactions of protonated peptides by means of a flow tube technique necessitates the introduction of these intact ions into the tube. The ability to combine electrospray ionization (ESI) with the flowing afterglow method has recently been demonstrated by Squires and his group [12]. We constructed a similar simple electrospray ionization source for our flow tube reactor and applied it to the study of reactions of GLY_2H^+ to be described here.

2. Experimental

We constructed a SIFT apparatus some years ago, which has been described in detail elsewhere [13]. This apparatus has been modified to work with an electrospray ionization source connected directly to the flow tube, as in the work of Poutsma et al. [12] and not through the injector quadrupole; reactant ions were thus not mass selected. Briefly, the SIFT consists of a flow reactor that is 123 cm in length and an inner diameter of 74 mm. A neutral reagent is introduced into the flow tube through either one of two ring inlets. Tylan mass flow controllers define the flow rate of the neutral reactant into the flow tube. The quadrupole mass analyzer is housed in a differentially pumped chamber that is separated from the flow tube by a skimmer with a 1.0 mm sampling orifice. Helium buffer gas enters the flow tube at the upstream end near an electron impact ion source through another Tylan flow controller. It is pumped through the tube by a Roots blower with flow velocities of up to about 9000 cm s^{-1} with typical pressures of a few tenths of a Torr.

The electrospray ion source was designed following [12]. A capillary tube serves as the interface between the electrospray and the helium flow reactor. Stainless steel tubes 15–31 cm in length and 0.05 or 0.10 cm inner diameter (i.d.) are employed. In some of the experiments, the tubes are resistively heated directly by 12 A at 3.5 V to evaporate the solvent. Heating the capillary was not found to be of critical importance for our experiments. Heated capillaries are encased in a glass tubing. The capillary protrudes through a short ceramic spacer that is affixed to the inner wall of the glass tube with epoxy adhesive, resulting in a vacuum-tight seal around the capillary. The entire assembly is inserted into the flow tube at a distance of ~96 cm from the sampling orifice, 135° to the direction of the helium flow, through an “O”-ring type vacuum fitting. A capillary tube of 0.05 cm i.d. introduces an air leak into the flow tube with a pressure of 0.07 Torr and a flow rate of 1.3 L/min (STP) which had to be added to the helium flow when determining rate constants. A capillary tube of 0.10 cm i.d. introduces an air flow of 3.0 L/min and an added pressure of 0.125 Torr. Ions are electrosprayed ~10 mm through ambient air into the grounded capillary tube from a 22 gauge platinum syringe needle biased at 4500–5000 V dc. Dilute solutions of the analyte of interest in a polar solvent are delivered to the electrospray needle at flow rates of 1–5 μL min^{-1} from a 1000 μL syringe mounted on a model 100 KD Scientific Syringe Pump.

The system was tested by sampling the electrospray produced from a 1×10^{-5} M solution of n-$Bu_4N^+Br^-$ in 50:50 (v/v) methanol/water. As before [12], the only significant peak in the spectrum was at m/z 242 due to n-Bu_4N^+ with an optimized ion current of 10 pA striking the ion aperture plate at the tip of the nose cone.

Second-order rate coefficients are obtained by monitoring the intensity of the primary ion decay as a function of the neutral gas B concentration introduced downstream. Product ion distributions are obtained by plotting the percentage of each product ion as a function of the gas B flow rate and extrapolating the resulting curves to zero flow rate. Product ion distributions are corrected via the measured mass discrimination factors of the detector quadrupole mass filter.

The ability to determine reaction rate coefficients for electrosprayed ions was tested by introducing ions which had previously been studied by mass separation using the injector quadrupole mass spectrometer. We have chosen for this purpose the ammonium complex of 12-crown-4 ether studied previously [14]. $Cr4NH_4^+$ ions were electrosprayed from a $12Cr4/NH_4Cl$ solution in acetone and allowed to react with dimethylether, methylamine, and dimethylamine. The resultant rate coefficients were in fair agreement with the ones reported previously [14].

Diglycine was a sample from SIGMA with a stated minimum purity of 99%. A 7.5×10^{-5} M solution of GLY_2 in 1% formic acid, 50% methanol, and 49% water was employed to electrospray the protonated diglycine. More highly acidic solutions that were more highly concentrated in GLY_2 were used in some experiments.

3. Results and discussion

Protonated diglycine, GLY_2H^+ (or G_2H^+), was allowed to react with the following base molecules B = NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, and CH_3OH. The major or sole primary product observed for all of these reactions was the ion complex, G_2BH^+, which is the mixed dimer. In the case of trimethylamine, the protonated base was observed as a primary product in addition to the complex. Secondary products include, in the case of the amines, the formation of a bis adduct of the amine to the protonated GLY_2, namely $G_2B_2H^+$, i.e. the mixed trimer, the protonated free dimer, B_2H^+ and, in the case of methanol, the adduct of dimethyl ether and G_2H^+, namely $G_2(CH_3OCH_3)H^+$.

Results for the reaction of the protonated dimer of glycine with trimethylamine are plotted in Fig. 1. The primary ion decay is linear on a semilogarithmic plot of the ion count rate as a function of the neutral flow rate. Effective second-order rate coefficients have been deduced from such plots and are summarized in Table 1. Four products are observed in the reaction of trimethylamine with GLY_2H^+: the protonated complex of GLY_2 with trimethylamine, protonated trimethylamine, the protonated dimer of trimethylamine, and the protonated complex of GLY_2 with the dimer of trimethylamine. Fig. 2 represents the percentage of the various product ions as a function of the trimethylamine flow rate. Extrapolation to zero flow rate demonstrates that protonated trimethylamine and the protonated complex of GLY_2 with trimethylamine are primary products, and the other two products are secondary ones. The scheme for this reaction is therefore:

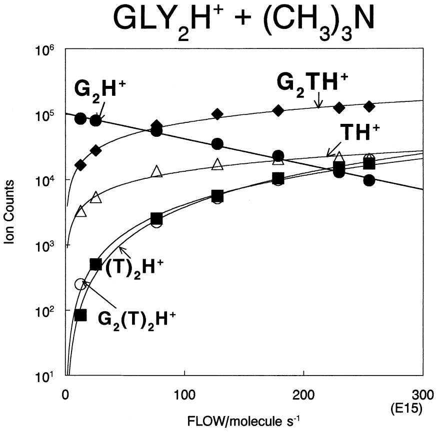

Fig. 1. Variation of primary and product ion count rates with trimethylamine flow rate for the reaction of protonated diglycine with trimethylamine. G_2H^+, protonated diglycine: line and filled circle; G_2TH^+, protonated mixed dimer of GLY_2 and trimethylamine: filled diamond; TH^+, protonated trimethylamine: open triangle; $(T)_2H^+$, protonated trimethylamine dimer: filled square; $G_2(T)_2H^+$, protonated trimer of GLY_2 and two trimethylamines: open circle.

Table 1
Ion/molecule reaction rate constants (in units of 10^{-9} cm^3/molecule sec) of GLY_2H^+ + B

B	k_{exp}	k_c	r_{eff}
NH_3	$k' = 0.3–1.3$ [a]	2.04	0.15–0.64
	$k'' = 0.004–0.024$ [a]		0.002–0.001
CH_3NH_2	1.44	1.61	0.9
$(CH_3)_2NH$	1.34	1.35	0.99
$(CH_3)_3N$	1.30	1.16	1
CH_3OH	0.047	1.81	0.026

[a] For the flow tube pressure range 0.1–0.4 Torr.

$$\mathrm{GLY_2H^+ + (CH_3)_3N \rightarrow GLY_2(CH_3)_3NH^+} \tag{1a}$$

$$\downarrow + \mathrm{(CH_3)_3N}$$

$$\longrightarrow \mathrm{GLY_2[(CH_3)_3N]_2H^+} \tag{2a}$$

$$\longrightarrow \mathrm{[(CH_3)_3N]_2H^+} \tag{2b}$$

$$\rightarrow \mathrm{(CH_3)_3NH^+} \tag{1b}$$

$$\downarrow + \mathrm{(CH_3)_3N}$$

$$\longrightarrow \mathrm{[(CH_3)_3N]_2H^+} \tag{2c}$$

No protonated base was observed as a product in any of the other systems. Even in the case of the trimethylamine reaction, the percentage of the protonated complex is in excess of 80% (see Fig. 2). There are several conflicting values for the proton affinity of diglycine in the literature [7a,15–17]. Because all of the reported values are lower than that of trimethylamine, PA(trimethylamine) = 225.1 kcal mol^{-1} [18], proton transfer from GLY_2H^+ to trimethylamine is obviously exothermic and should take place under the thermal conditions of the flow tube experiment. If PA(GLY_2) = 219.1 ± 0.8 kcal mol^{-1} [15], then proton transfers to methanol (PA = 181.9 kcal mol^{-1}), ammonia (PA = 204 kcal mol^{-1}), and methylamine (PA = 214.1 kcal mol^{-1}) are endothermic and should not take place, whereas proton transfer to dimethylamine (PA = 220.6 kcal mol^{-1}) is nearly thermoneutral or slightly exothermic and is not observed since collisional stabilization of the complex is preferred. Alternatively, our data might indicate that the proton affinity of diglycine is lower than that of trimethylamine but higher than that of dimethylamine, i.e. $PA[(CH_3)_2NH] < PA(GLY_2) < PA[(CH_3)_3N]$, in agreement with Zhang et al., according to which PA(GLY_2) = 223.4 kcal mol^{-1} [17].

The reaction scheme suggested on the basis of our data for the GLY_2H^+ reaction with methanol is as follows:

$$\mathrm{GLY_2H^+ + CH_3OH \rightarrow GLY_2(CH_3OH)H^+} \tag{3}$$

$$\downarrow + \mathrm{CH_3OH}$$

$$\longrightarrow \mathrm{GLY_2(CH_3OCH_3)H^+ + H_2O} \tag{4}$$

H-D exchange between protonated glycine oligomers and ammonia has been proposed to take place following proton transfer to ammonia within the collision complex—the so-called “onium ion mechanism” [5]. For those reagents, e.g. water, whose proton affinities are too low to form solvated onium ion intermediates, a relay mechanism was proposed in which the reagent shuttles a proton from the N-terminus to a slightly less basic sight in the molecule. The situation regarding methanol remained ambiguous. Nibbering and coworkers [7a] came to the conclusion that even in the case of D_2O the proton can be transferred to the reagent within the complex. If this is the case, then proton transfer within the complex should certainly take place also for methanol, whose proton affinity is considerably higher than that of water. Formation of protonated dimethylether with concomitant elimination of water is a well known reaction of protonated methanol with neutral methanol, whose mechanism is via an S_N2 displacement [19]. The observation of reaction (4) within the (GLY_2-CH_3OH)H^+ complex is of great significance, because it indicates that proton transfer to methanol has indeed taken place.

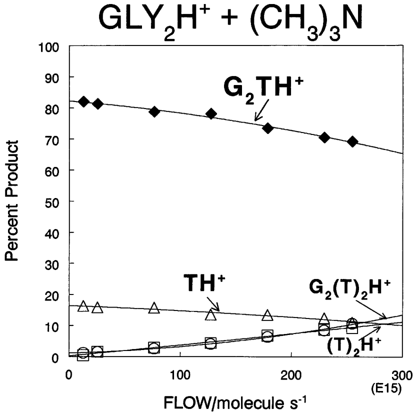

Fig. 2. Product ion distribution as a function of trimethylamine flow rate for the reaction of protonated diglycine with trimethylamine.

Experimental rate coefficients, k_{exp} can be compared with ion-polar molecule collision rate constants, k_c calculated according to the parametrized expression of Su and Chesnavich [20]. This has been done and results for k_c and for the reaction efficiencies, $r_{\text{eff}} = k_{\text{exp}}/k_c$ are included in Table 1. Reaction efficiencies are equal to, or nearly equal to, unity for trimethylamine, dimethylamine, and methylamine but are less than one and show pressure dependence for methanol and ammonia, whose deuterated isotopomers are the H-D exchange reagents discussed above. Ion/molecule association rate coefficients are known to be pressure dependent [21–23]. In the high pressure limit the association rates equal the collision (capture) rates, whereas at low pressures fall-off effects come into play and the association rate becomes much less than the capture rate. The overall process,

$$\text{GLY}_2\text{H}^+ + \text{NH}_3 \xrightarrow{\text{M}} \text{GLY}_2\text{NH}_4^+ \tag{5}$$

is considered to proceed in two consecutive steps:

$$\text{GLY}_2\text{H}^+ + \text{NH}_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{GLY}_2\text{NH}_4^+)^* \tag{6a}$$

$$(\text{GLY}_2\text{NH}_4^+)^* + \text{M} \xrightarrow{k_2} \text{GLY}_2\text{NH}_4^+ + \text{M} \tag{6b}$$

In the first step, the excited, chemically activated intermediate complex ion is formed, which in the case of reaction with ND$_3$, would be responsible for the H-D exchange. It is formed with a rate coefficient k_1 which is calculable ($k_1 = 2.04 \times 10^{-9}$ cm^3/molecule s; see Table 1) on the basis of the Su and Chesnavich parametrized equation [20]. The chemically activated intermediate dissociates back to the reactants with a unimolecular rate coefficient k_{-1}. In the second step the complex can be stabilized in collisions with third body particles, M, which in our case are He, N$_2$, and O$_2$, with a rate coefficient $k_2 = \beta \cdot k_{c2}$ where k_{c2} is the collisional rate coefficient of the reaction of the chemically activated complex with M, and β is the stabilization efficiency, $\beta \leq 1$. Application of the steady state approximation to (GLY$_2$NH$_4^+$)* yields an effective binary rate coefficient, k_{eff},

$$k_{\text{eff}} = k_1 \frac{k_2[M]}{k_{-1} + k_2[M]} \tag{7}$$

In the high pressure limit, $k_2[\text{M}] \gg k_{-1}$ and $k_{\text{eff}} = k_1$. Inspection of Table 1 demonstrates that the reactions of GLY$_2$H$^+$ with trimethylamine, dimethylamine, and possibly also methylamine are in their high pressure limit under the pressures employed in the flow tube (0.1–0.4 Torr) but the reactions with ammonia and methanol are not. The ammonia system was studied in greater detail. Typical results for the primary ion decay as a function of ammonia flow rate are presented in Fig. 3. On a semilogarithmic scale the plot is clearly made up of two linear sections and can be analyzed in terms of two, quite different effective rate constants each of which is pressure dependent (see Table 1). Eq. (7) can be recast into

$$1/k_{\text{eff}} = 1/k_1 + (k_{-1}/k_1k_2)1/[\text{M}] \tag{8}$$

Fig. 4 presents a plot of $1/k_{\text{eff}}$ as a function of 1/[M] for the slow effective decay rate constants obtained from plots of the type presented in Fig. 3. Substituting the calculated values for k_1 and k_2 into the slope deduced for Fig. 4 yields a value for the unimolecular rate constant, k_{-1}. This has been done for the pressure

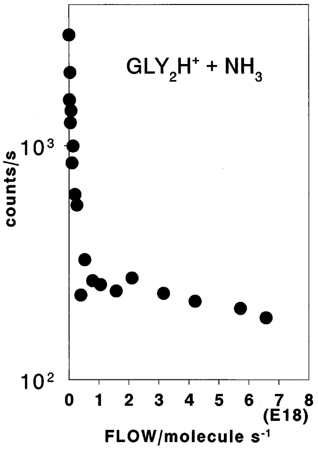

Fig. 3. Semilogarithmic plot of the decay of primary ions as a function of the neutral flow rate for the reaction of protonated diglycine with ammonia at a total flow rate of the carrier gas of 10.2 STP L/min and a flow tube pressure of 0.4 Torr.

dependence of the slow, as well as the fast, effective decay rate constants in the ammonia system. As before, $k_1 = 2.04 \times 10^{-9}$ cm^3/molecule s; furthermore $k_{c2} = 5.7 \times 10^{-10}$ cm^3/molecule s (average value for helium and air) and if $\beta = 0.2–0.5$, then two unimolecular rate constants are deduced as follows: $k_{-1,\text{slow}} = (3–7) \times 10^6$ s^{-1} (from the fast decay of the complex, Fig. 3) and $k_{-1,\text{fast}} = (2–5) \times 10^8$ s^{-1} (from the slow decay component).

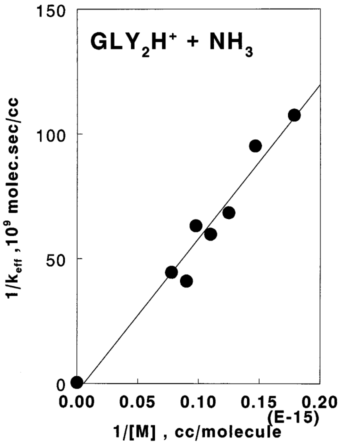

Fig. 4. Reciprocal effective binary rate coefficient as a function of reciprocal third body concentration for the reaction of protonated diglycine with ammonia; M is a mixture of He, O_2, and N_2.

The two slopes observed in Fig. 3 may be due to an artifact. Since no such artifacts were observed for the other systems (e.g. for trimethylamine, etc.) the results are considered to be real. They may be due to two isomeric structures of the intermediate chemically activated complex. The two isomers can be: (1) The GLY$_2$H$^+$-NH$_3$ ion-dipole complex, and (2) the hydrogen-bonded GLY$_2$NH$_4^+$ complex, as suggested in the "onium-ion mechanism" [5]. Alternatively, the two isomers may be two GLY$_2$-NH$_4^+$ complexes, hydrogen bonded at different positions [7] or two complexes of GLY$_2$H$^+$ protonated at different sites whose protonation site does not vary during the complexation and back reaction. Photo-electron photo-ion coincidence (PEPICO) experiments have shown a number of isomeric systems which dissociate via two-component decay kinetics [24]. The potential energy profile suggested for the "onium-ion mechanism" [5] is a two-well, one-product channel potential energy profile of the kind which leads to two-component decay kinetics. If the deep well is accessed in the ionization process, only the slow rate is observed. However, in the ion/molecule collision process the shallow well of the ion-dipole complex is formed first. As a result, k_{-1} should demonstrate two-component kinetics in a similar fashion to the PEPICO experiments. Each of the k_{-1} components is an algebraic combination of elementary rate constants [24], involving the forward and backward isomerization steps and the back dissociation from the shallow well of the ion-dipole complex, to the original reactants. Ab initio calculations of the potential energy surface, followed by RRKM calculations on such a surface, are planned in the future in order to model the experimental results.

4. Conclusions

(1) Ion/molecule reactions of protonated dipeptides can be studied under thermal conditions at relatively high pressures of a flow reactor. Extension of the present study to larger polyprotonated protein systems is foreseen.

(2) Protonated diglycine undergoes reversible complexation reactions with reagents such as NH_3

and CH_3OH, whose deuterated isotopomers are well known H-D exchange reagents.

(3) Proton transfer from GLY_2H^+ to methanol occurs within the complex. This has been proven through the observation of a well known ion/molecule reaction of protonated methanol which occurs within the complex.

(4) The effective binary complexation rate constant of GLY_2H^+ with ammonia demonstrates two-component decay kinetics of the kind which is well known for unimolecular systems undergoing isomerization and dissociation in competition. This behaviour is ascribed to isomerization within the complex that is in competition with the back dissociation reaction. The identity of the two isomers remains an open question, but they could conceivably be the ion/dipole complex and the hydrogen bonded ammonium ion complex, respectively.

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