the angular part of the lone pair repulsion.

The calculated differences in C–H bond lengths are in good agreement with previous calculations,[21] and with experimental values.[3] Our calculations predict equal bond distances for CH_3NO, but experimental data to test the prediction are not yet available.

Conclusions

The methyl group tilt in all of the conformations, both equilibrium and artificially constrained, of all of the compounds examined can be explained as the consequence of repulsion between the C–H bonds of the methyl group and the bonds on the adjacent atom. The repulsion between C–H and either an N–H, O–H, or N=O bond is greater than the repulsion between the C–H bond and a lone pair. The molecules adopt the configuration with the smallest total bond-bond repulsion. Since this often leads to a situation where one bond is repelled more strongly than the other two, the result is a tilt of the methyl group. The repulsion between the C–H bond and the lone pairs is of little importance because in the cases examined the lone pairs either have a high degree of p symmetry and therefore repel on both sides of the nucleus, as in methanol and methylamine, or form an angle with the C–X bond larger than does the bonded atom on X, as in nitrosomethane.

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References and Notes

(1) (a) Department of Chemistry, University of Tromsø, Tromsø, Norway; (b) Institute for General and Inorganic Chemistry, Eötvös Lorand University, Budapest, Hungary.

(2) U. Blukis, P. H. Kasai, and R. J. Meyers, *J. Chem. Phys.*, **38**, 2753 (1963).

(3) D. C. McKean, J. L. Duncan, and L. Batt, *Spectrochim. Acta, Part A*, **29**, 1037 (1973).

(4) W. A. Latham, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, 11, 175 (1974).

(5) C. W. Kenn, R. M. Pilzer, and O. J. Sovers, *J. Chem. Phys.*, **60**, 3583 (1974).

(6) H. B. Schlegel, S. Wolfe, and F. Bernardi, in press.

(7) P. Pulay and F. Török, *J. Mol. Struct.*, **29**, 239 (1975).

(8) W. H. Paine and L. C. Allen, in press.

(9) S. Skaarup, L. L. Griffin, and J. E. Boggs, *J. Am. Chem. Soc.*, **98**, 3140 (1976).

(10) (a) P. W. Payne and L. C. Allen, in press; (b) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967); (c) C. Peclezen and K. Morokuma, *ibid.*, **48**, 3941 (1967).

(11) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(12) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 209 (1970). During the studies it was discovered that one of the exponents for a carbon s orbital was erroneously given the value 43.8498 instead of 45.8498 suggested by Roos and Siegbahn. A test calculation with the latter value showed a slight lowering of energy but no change in the geometry or the forces. We therefore used the former value in all the calculations.

(13) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

(14) (a) P. Pulay, *Mol. Phys.*, **17**, 197 (1969); (b) *ibid.*, **18**, 473 (1969).

(15) E. Flood and J. E. Boggs, *J. Mol. Struct.*, **34**, 147 (1976).

(16) S. E. Boys, "Quantum Theory of Atoms, Molecules and the Solid State", P. O. Löwdin, Ed., Academic Press, New York, N.Y., 1966, p 253.

(17) (a) A. P. Cox, University of Bristol, private communication; (b) D. Coffey, C. O. Britt, and J. E. Boggs, *J. Chem. Phys.*, **49**, 591 (1968).

(18) R. M. Lees and J. G. Baker, *J. Chem. Phys.*, **48**, 5299 (1968).

(19) M. A. Robb, W. J. Haines, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **95**, 42 (1973).

(20) P. A. Christiansen and W. E. Palke, *Chem. Phys. Lett.*, **31**, 462 (1975).

(21) S. Wolfe, B. Schlegel, M. Whangbo, and F. Bernardi, *Can. J. Chem.*, **52**, 3787 (1974).

Protonation Processes of Unusual Exothermicity

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Abstract: The protonation of guanidine and biguanide is more exothermic by 25 and 70%, respectively, than the neutralization of OH^-, the strongest base in aqueous solution. The effect is caused by the symmetrization of the mesomeric molecules during the process (resonance energy). The protonated base molecules are also more rigid, which shows up in unusually low and even negative entropy changes.

The most exothermic neutralization processes occurring in aqueous solution have reaction enthalpies not exceeding 60 kJ/mol. The protonation of OH^-, the strongest base in water, with $\Delta H = -56$ kJ/mol, is close to that limit. Although ammonia and aliphatic amines are much less basic than OH^-, their protonation enthalpies are in the same range and for some of them even slightly more negative. On the other hand, surprisingly small enthalpy changes are found in the neutralization of doubly charged anionic strong bases. The strongly exergonic character of these neutralizations (large and negative $\Delta G = -2.3RTpK = \Delta H - T\Delta S$) is, to a considerable extent, caused by the large and positive entropy change during the reaction (see Table I).

Interest in the metal complexes of biguanide made it necessary to determine the enthalpy of its protonation. Thereby we discovered that this strong base (pK = 13.0) is the absolute champion with respect to the exothermicity of its neutralization. This result motivated us to investigate the parent compound guanidine as well and indeed, the neutralization of this base (pK = 13.5) is also unusually exothermic.

Experimental Section

The data of lines 1–6 in Table I have been taken from the literature.[3] The enthalpies of the last three reactions have been determined using a flow microcalorimeter LKB 10700-1 following a described procedure.[4] The solutions of the reactants were injected by high precision burettes (Mettler DV 105).

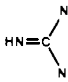
Guanidinium chloride (Erba, Milano) was recrystallized from ethanol. A reliable pK value for guanidine is known at the ionic strength $I = 1$ M $NaClO_4$,[5] which was used to calculate the equilibrium concentrations before and after mixing a 0.05 M solution of [HGuan]Cl adjusted to $I = 1$ M with $NaClO_4$ and 1 M NaOH in various ratios.

Biguanide (Aldrich-Europe) was obtained in the form of the crystalline free base from *N,N*-dimethylformamide. The two basicity constants are known at the ionic strength $I = 0.1$ M (KCl)[6] and were used to calculate the equilibrium concentrations before and after mixing the solutions of the reactants in the two series of experiments performed. In the first series, a 0.01 M solution of biguanide and 0.005 M HCl was mixed in various ratios with a 0.015 M solution of HCl. In the second series 0.007 M biguanide and 0.014 M HCl was mixed with 0.1 M KOH in various ratios. All solutions were adjusted to $I = 0.1$ M with KCl.

For the calculations exact values of the enthalpy of neutralization of OH^- were needed and have been determined in the two media in separate experiments. The knowledge of the equilibria concentrations for each species before and after mixing allows the splitting of the recorded calorimetric response into the various enthalpic contributions. The set of linear equations was solved by a least-squares method in minimizing the difference between experimental and calculated heat effect.

Results and Discussion

On protonation the base **1** becomes a symmetrical cation $C(NH_2)_3^+$ with three equivalent amino groups and the π electrons delocalized over the entire molecule.[10] The resonance energy gained is mainly responsible for the strongly basic character of guanidine as well as the large and negative enthalpy change during its protonation.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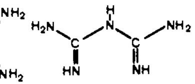
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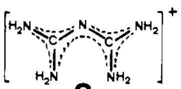
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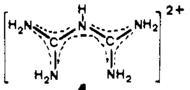
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The anion CO_3^{2-} is the oxygen analogue of the guanidinium cation, but during its protonation, the delocalization of the π electrons is reduced. The negative charge of the bicarbonate no longer resides on all three, but only on the two unprotonated oxygen atoms. In contrast to guanidine the protonation of carbonate must be accompanied by a loss of resonance energy, making the reaction less exothermic.

However, the protonation of guanidine and of carbonate differ drastically in the entropy of the reaction. When the proton is transferred from the aqueous hydronium ion (possibly $H_9O_4^+$)[11] to the uncharged base, the number of ions in solution remains unaltered, but the localized charge of the hydrogen ion will be more effective in orienting the neighboring water molecules than the delocalized charge of $C(NH_2)_3^+$. The effect of the disappearance of the ion H^+ on ΔS of protonation processes can be estimated from the entropy change observed in the first reaction of Table I. The reactant H^+ may be considered as a site with a surplus proton and the reactant OH^- as a site with a missing proton within the water structure. Both ions order the solvent structure to about the same extent, giving rise to an entropy increase of about 56 J/K mol for each vanishing site. In the protonation of guanidine the hydrogen ion is replaced by the less order producing $C(NH_2)_3^+$, which results in a positive entropy change. This change is somewhat reduced because the localized double bond of **1** gets distributed around the molecule, thus preventing the free rotation of the NH_2 groups. The small positive value of ΔS observed is the difference of the two effects.

The protonation of carbonate is very different because of the accompanying partial compensation of charges. Two ions disappear which were both very effective in orienting the surrounding water molecules, the H^+ ion because it fits into the solvent structure and CO_3^{2-} because of its double negative charge. The anion HCO_3^-, on the other hand, is not expected to be especially order producing. When carbonate is protonated a considerable liberation of water molecules will take place. This process not only makes ΔS of the reaction strongly positive, but also reduces further the exothermicity $-\Delta H$ because of the energy that the at least partially liberated H_2O molecules will take up from their surroundings.

Table I. Thermodynamic Quantities in Aqueous Solution[7] (−25 °C)

Process	$-\Delta G$, kJ/mol	$-\Delta H$, kJ/mol	ΔS, J/K mol
$H^+ + OH^- \rightleftarrows H_2O$[a]	89	56	111
$H^+ + NH_3 \rightleftarrows NH_4^+$	53	52	3
$H^+ + RNH_2 \rightleftarrows RNH_3^+$	50-60	48-58	5-15
$H^+ + py \rightleftarrows Hpy^+$	29	20	30
$H^+ + S^{2-} \rightleftarrows HS^-$	80	50	100
$H^+ + CO_3^{2-} \rightleftarrows HCO_3^-$	58	15	146
$H^+ + Guan \rightleftarrows HGuan^+$	78	76	8
$H^+ + Big \rightleftarrows HBig^+$	74	95	−71
$H^+ + HBig^+ \rightleftarrows H_2Big^{2+}$	17	21	−13

[a] Log $K = 14 + \log 55$; R = alkyl; py = pyridine; Guan = guanidine; Big = biguanide.

The production of heat in the protonation of biguanide is fantastically high, $-\Delta H$ being more than 60% larger than the enthalpy of the most exothermic protonation known up to the present. That biguanide is not a stronger base is due to the large entropy loss during protonation. No charge compensation occurs and the product $HBig^+$ is not expected to be more effective than H^+ in immobilizing the neighboring solvent molecules. The strongly negative value of ΔS, therefore, tells us that a very flexible base molecule is converted into a very rigid cation (see formulas **2** and **3**). Structure **2** is the formula usually given to biguanide and contains well localized double bonds C=NH, so that rotation about the remaining single bonds can take place freely, making **2** flexible. When we assume that the protonation of one of the imino groups of **2** induces a migration of a proton from the bridging nitrogen to the second NH, we arrive at structure **3**, for which five canonical formulas can be written, four of them being equivalent. All the C-N bonds in **3** have pronounced double bond character, which makes the molecule very rigid. The four π electrons are delocalized over a larger area than in $C(NH_2)_3^+$, so that the resonance energy must also be larger. This large resonance energy explains the unusual exothermicity of the protonation of biguanide as well as the unusual entropy loss during the reaction.

Biguanide adds a second proton at low pH values ($pK = 3.0$) and structure **4** is suggested for the product H_2Big^{2+}, according to which the second proton is bound by the bridging nitrogen of **3**, which leaves the symmetry unchanged. This bridging nitrogen of **3** is comparable with the nitrogen of pyridine and indeed, the same amount of heat is produced in the reactions on line 4 and line 9 of Table I. However, the entropy change in the protonation of pyridine is positive and negative in the protonation of $HBig^+$, which means that the singly charged Hpy^+ is less effective than H^+ and the doubly charged H_2Big^{2+} is somewhat more effective in ordering nearby solvent molecules.

References and Notes

(1) Istituto di Chimica Generale e Inorganica e Laboratorio C.N.R.
(2) Anorganische Chemie ETH.
(3) "Stability Constants of Metal Complexes", *Chem. Soc., Spec. Publ.*, **No.** 17 (1964); **No. 25** (1971). Data were also taken from: J. J. Christensen et al., *J. Chem. Soc. A*, 1212 (1969); L. Sacconi et al., *J. Am. Chem. Soc.*, **82,** 3831 (1960); J. W. Kury et al., *J. Electrochem. Soc.*, **100,** 468 (1953).
(4) C. Blanchini, L. Fabbrizzi, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1036 (1975).
(5) T. H. Wirth and N. Davidson, *J. Am. Chem. Soc.*, **86,** 4325 (1964).
(6) G. Schwarzenbach and G. Anderegg, *Pharm. Acta Helv.*, **38,** 547 (1963).
(7) To account for the translational entropy loss in the course of associations taking place in solution, such as the reactions in Table I, the use of the so-called unitary quantities has been recommended.[8] The ΔS values of

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the table would be increased by the cratic entropy $S_c = R \ln 55$ (= 33 J/K mol) and make ΔG more negative by 10 kJ/mol. Because we doubt[9] whether it is correct to replace a translational entropy by a mixing entropy, such as S_c, this correction was not applied.
(8) R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill, New York, N.Y., 1953.
(9) G. Schwarzenbach, *Pure Appl. Chem.*, **24**, 307 (1970).
(10) D. J. Haas, D. R. Harris, and H. H. Miller, *Acta Crystallogr.*, **19**, 676 (1965).
(11) M. Eigen, *Angew. Chem.*, **75**, 489 (1963).

Thermal and Nonthermal Decompositions, Eliminative Ionic Polymerization, and Negative Temperature Coefficients in the i-C_4H_{10}–Benzyl Acetate System. A Time-Resolved Chemical Ionization Mass Spectrometric Study

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Abstract: The i-C_4H_{10}-benzyl acetate (BzOAc) reaction system was investigated by pulsed, time-resolved chemical ionization mass spectrometry. The following novel observations were made: (a) The rate constant, k_f, for i-C_4H_{10} + BzOAc → products decreases from 24×10^{-10} at 320 K to 0.61×10^{-10} cm^3/mol s at 520 K, with a negative temperature dependence of $k_f \propto T^{-6}$–T^{-10}. (b) The Bz^+ and $BzOAcH^+$ ions are formed from the competitive fast decomposition of $(t\text{-}C_4H_9{}^+\cdot BzOAc)^*$; the difference between the activation energies for the two processes is 13.6 kcal/mol. (c) The Bz^+ ion initiates a sequence of eliminative ionic polymerization reactions of the general form $(C_7H_7\cdot(n-1)C_7H_6)^+ + BzOAc \rightarrow (C_7H_7\cdot nC_7H_6)^+ + HOAc$ (n = 0–4). The process appears to proceed at about collision rate and without an activation energy. (d) The polymer ions $(C_7H_7\cdot C_7H_6)^+$, $(C_7H_7\cdot 2C_7H_6)^+$, and $(C_7H_7\cdot 3C_7H_6)^+$ undergo thermal decomposition with the loss of H_2, possibly to form protonated anthracene ions. These reactions are in competition with further polymerization. The rate constant for thermal H_2 loss, $(C_7H_7\cdot C_7H_6)^+ \rightarrow C_{14}H_{11}{}^+ + H_2$, at 470 K is 1.3×10^4 s^{-1}. (e) The $C_7H_7{}^+$ ion formed from BzOAc in CH_4 protonates BzOAc; that formed in i-C_4H_{10} does not. (f) The thermodynamic values for $BzOAcH^+ + BzOAc \rightarrow (BzOAc)_2H^+$ are $\Delta H° = -28.9$ kcal/mol, $\Delta S° = -34.7$ eu. (g) Continuous ionization CIMS appears to correspond to ions formed in 5–15 μs reaction time. (h) Analytical chemical ionization experiments using i-C_4H_{10} should be performed at the lowest temperature compatible with other experimental requirements.

Since the introduction of chemical ionization mass spectrometry (CIMS) about a decade ago,[1,2] the technique has been applied to the analysis of a large variety of substances. Despite the widespread application, the mechanism and kinetics of the processes leading to the observed CIMS spectra of complex molecules have scarcely been investigated. One of the earlier attempts to make such an investigation was directed at the examination of temperature and pressure effects in the i-C_4H_{10} CIMS spectra of benzyl acetate (BzOAc) and related compounds.[3-6] The most significant ions observed in the i-C_4H_{10}-BzOAc system were Bz^+($C_7H_7{}^+$, m/e 91), $BzOAcH^+$ (m/e 151), $(BzOAc)_2H^+$ (m/e 301), $Bz^+\cdot BzOAc$ (m/e 241), and $Bz^+\cdot BzOAc$-HOAc (m/e 181). The kinetic studies were directed mostly at the formation of the Bz^+ fragment ion and MH^+-HOAc fragment ions in other acetates. In that work, which was done in this laboratory using a conventional continuous ionization technique, it was assumed that ions are formed in the ion source in a thin ribbon at the level of the entrance of the ionizing electron beam to the ion source. These ions were then assumed to undergo chemical reactions while diffusing from the ionization area to the ion exit slit. The reaction sequence of major interest was assumed to be the formation of protonated quasi-molecular ions (MH^+) by proton transfer from t-$C_4H_9{}^+$ to the additive molecules, followed by the thermal decomposition of the MH^+ ions.

Following the introduction of pulsed ionization technique in our laboratory, we undertook to reexamine the mechanism of reactions in the i-C_4H_{10}-BzOAc system. As will be seen, the results require us to modify our idea about the mechanism of the formation of the protonated molecular ion and the fragment ions; they lead to the observation of previously unobserved reactions; and they yield more reliable measurements of rate and equilibrium constants for the principal reactions in this CIMS system. Thus the results illustrate the use of the pulsed technique to clarify the mechanisms of complex CIMS processes.

Experimental Section

The present work was conducted on the Rockefeller University chemical physics mass spectrometer used in the pulsed mode.[7,8] The important feature of this technique is that ions are generated by a short pulse of ionizing electrons, usually of 8–20-μs duration in this work, and the intensities of the ions issuing from the source are recorded explicitly as a function of the residence times (i.e., reaction times) of the ions in the ionization chamber. Assumptions about the spatial distribution of initial ionization and about ion residence times, which were required in the previous work with continuous ionization, are not necessary, and the change of ion intensities with reaction time is directly observable.

Mixtures of benzyl acetate (BzOAc) in i-C_4H_{10} or CH_4 were prepared in a heated bulb, and the mixture was allowed to flow into the source in a stream of additional reactant gas. The technique was described in a previous publication.[3] Usually 1–50 μL of BzOAc was used, leading to a partial pressure of 0.15–7.5 mTorr of BzOAc in 0.5–1.0 Torr of reactant gas in the source. Materials used in this study were benzyl acetate and 2,6-dimethylaniline, MCB, purity >99%; isobutane, Matheson, instrumental grade; methane, Matheson, ultra high purity grade.

Results and Discussions

1. Time-Resolved CIMS of the i-C_4H_{10}–BzOAc System. Examples of time-resolved CIMS in the i-C_4H_{10}–BzOAc