of methanol during the initial induction period, perhaps by protons or methyloxonium ions, which function as methyl cation equivalents; later, as olefins are generated, carbocations (from protonation of olefins) must become the hydride acceptors. This suggestion is consistent with the substantial fraction of fully saturated hydrocarbons produced by these reactions.[5] Such a product spectrum would obviously be impossible without a net source of hydrogen.

The CO-catalyzed mechanism explains the connection between propene and ethylene formation.[13c,14c,d] It further suggests several simple experimental tests, of which we have performed the first and most obvious. We have searched for exchange between the acidic *H*OX and the methoxy HCH_2OX protons and found none by running the Pearson reaction with CD_3OD. This observation suggests that for an oxonium methylide to be important in this reaction *it must be methylated at a much greater rate than it is reprotonated*. Since this process is kinetically unlikely in the unstructured PPA solution, we conclude from our experiments that the oxonium methylide mechanism is not operating in the 200 °C PPA-catalyzed transformation of methanol into hydrocarbons. We are currently conducting experiments to determine whether added CO or CO precursors significantly alter the timing and sequence of appearance of reaction products in the Pearson reaction. In addition, we are pursuing a collaborative effort to study the methylation reactions of CO and ketene by methyl cation donors such as protonated methanol in the gas phase.

Summary

We have proposed a new mechanism to account for the initial transformation of methanol into hydrocarbons by acidic oxide catalysts such as H-ZSM-5 or PPA. From their similarities in products, we infer that the Mobil process and the Pearson reaction occur by mechanisms that are essentially the same, in spite of the different compositions and structures of the catalysts. A familiar presence in the zeolite systems, CO is now seen as the active catalyst, at least in the reaction's early phases. H-ZSM-5 or PPA are relegated to the simple role of medium to strong Brönsted acids, which promote dehydration, are weakly able to oxidize methanol to CO in the initial period, and retain CO in the reacting medium. Our results for the Pearson reaction support this picture, principally by casting doubt on the oxonium ylide pathway. On thermochemical grounds and by the absence of observable OH/CH exchange in the methoxyl groups derived from methanol, the intermediacy of oxonium methylides in these MTG reactions seems highly unlikely. The story is less exciting without the relatively exotic oxonium ylides. It is more thermochemically reasonable, however, and it reaffirms the dominance of the carbonyl group in organic chemistry. In place of framework or phosphate oxygen and oxonium methylides, carbon monoxide and ketene are seen as the catalytic activating group and nucleophilic carbon species, respectively. By revealing the central role of CO, a gaseous byproduct, this new mechanistic scheme introduces a fresh paradigm for the design of catalysts and control of reactions.

Acknowledgment. Professor Donald Pearson has been outstandingly helpful in excavating and sharing his original PPA results; we are most grateful for his encouragement and wisdom. J.E.J. thanks the Camille and Henry Dreyfus foundation for a Distinguished Young Faculty award and Michigan State University for generous startup support. Professors G. A. Olah, J. F. Haw, and J. F. Liebman offered useful data, references, and suggestions; Dr. Evelyn Jackson assisted with our early multinuclear NMR work; Professor Michael Rathke contributed insights on phosphorus chemistry; and an enthusiastic freshman, Mike Vethacke, tested the earlier experimental designs that led to our decision to examine the Pearson reaction in situ by NMR.

Gas-Phase Proton Affinity of Deoxyribonucleosides and Related Nucleobases by Fast Atom Bombardment Tandem Mass Spectrometry

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Abstract: The proton affinities (PA) of the deoxynucleosides and nucleobases present in DNA's have been determined from the kinetics of the gas-phase unimolecular dissociations of their proton-bound hetero-complexes with amines of known PA. The clusters have been formed by fast-atom-bombardment mass spectrometry from different matrices, whose effect has been evaluated. The experimentally determined order dG > dA ≅ dC ≫ dT differs from that of the corresponding pyrimidine and purine bases, Gua > Cyt > Ade ≫ Thy, and from that of the same nucleosides in aqueous solutions.

Introduction

Acid–base equilibria involving nucleic acid components have been widely investigated in polar and apolar solvents by spectroscopic means.[1] The determination of the pK_a values and of the protonation sites of nucleobases and nucleosides contributed to the understanding of the chemical processes undergone by DNA molecules in the condensed phase. The availability of desorption ionization (DI) methods in mass spectrometry (MS)[2,3] has favored a rapid growth of gas-phase investigations in the field of nucleic acid chemistry.[4-8] Moreover, the properties of the DI method known as fast-atom-bombardment (FAB)[9] have opened new

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frontiers to the chemistry of biological molecules allowing the formation and detection of protonated clusters of amino acids,[10] deoxynucleosides,[11] and amino acid–nucleoside[12] pairs. The evaluation of the gas-phase chemistry of the protonated clusters containing nucleic acid moieties requires the knowledge of the proton affinity (PA) values of the four DNA nucleosides. Furthermore, the estimation of these parameters in a hydrophobic environment such as high vacuum,[12] could lead to a better understanding of the intrinsic properties of such molecules in the isolated state, providing data unaffected by the solvent properties. The PA values of the nucleobases thymine (Thy), cytosine (Cyt), and adenine (Ade) have been experimentally determined by high-pressure mass spectrometry.[13] Chemical ionization experiments have provided also an estimation of the gas-phase basicity of some ribonucleosides;[14] however, experimental values do not exist either for the deoxyribonucleosides (dN), deoxythymidine (dT), deoxyadenosine (dA), deoxycytidine (dC), and deoxyguanosine (dG), present in DNA molecules, or for the nucleobase guanine (Gua).

Results and Discussion

Relative gas-phase proton affinities can be determined from the rates of the competing unimolecular dissociations of proton-bound dimers.[15,16] This kinetic method is an alternative to the thermodynamic approach[17] and has provided data in excellent agreement with those obtained by equilibrium measurements. It can be applied to involatile or thermally labile molecules by means of the available DI methods. The kinetic approach has been, in fact, employed in the determination of the PA scale of natural amino acids from the unimolecular dissociations of their proton-bound complexes produced by FAB.[10,18] The PA values obtained from the dissociation of proton-bound pairs may differ from those evaluated from equilibrium measurements when the sites through which hydrogen bonding occurs in the clusters are different from the protonation sites of the free bases. Some limitations of the methodology have been clearly addressed in the original application;[15,16] they, however, are counterbalanced by many advantages which include the possibility of discriminating among systems whose PA's differ by less than 0.1–0.2 kcal/mol.

Nucleic acid components such as nucleosides and nucleobases are characterized by the presence of multiple protonation sites; therefore, if dimer formation occurs under conditions of kinetic rather than thermodynamic control, it may be expected that their gas-phase unimolecular dissociations provide PA data that cannot be related to the most stable protonated forms of the examined species. The production of secondary organic ions by keV particle bombardment cannot adequately be explained by binary-elastic collisional sputtering.[19] According to theories recently developed,[3] the ion emission may be better described as involving processes approaching thermal equilibrium. Experimental evidences have been presented showing that the formation of protonated species by FAB is followed by nonreactive collisions which thermalize the ions.[20] Moreover, equilibrium constants have been obtained from a number of chemical and enzymatic equilibria investigated by FAB, which were consistent with those verified in solution experiments.[21,22] Therefore, it is expected that, under appropriate conditions and by applying the kinetic method referred to above, protonated heterocomplexes involving nucleic acid components could provide PA values that pertain to the most stable protonated forms of the examined species. By analogy with the amino acid experiments[10,18] these parameters might be obtained from the dissociations of proton-bound complexes formed by two nucleoside or nucleobase components; however, in this conditions multiple hydrogen-bonded species are produced.[11,13] This multicenter interaction can affect the determination of the PA values by the kinetic approach.

Therefore, the PA order of deoxynucleosides (dN) was evaluated from the unimolecular dissociations of $[dN+a+H]^+$ species produced by FAB from dN solutions containing appropriate amines (a) of known PA's (eqs 1a and 1b). Hindered amines were chosen as reference compounds to minimize the possibility of forming multiple hydrogen-bonded species.

$$dN\cdots H^+\cdots a \rightarrow [dN+H]^+ + a \qquad (1a)$$

$$dN\cdots H^+\cdots a \rightarrow dN + [a+H]^+ \qquad (1b)$$

This approach has the property that the determination of the relative basicity of the four DNA nucleosides as well as an accurate estimation of their absolute PA value can be gathered from the dissociations of the appropriate heterocomplexes (eqs 1a and 1b), if the bracketing with amines of known PA is carried out. A further advantage of the FAB-bracketing method is that the addition of the second base component (eqs 1a and 1b) directly to the solution of the species whose PA is to be determined avoids any problem due to the vaporization of the reference base. The rate constant (k) of a given unimolecular process near the threshold energy for fragmentation can be related to the critical energy (E_0) and to the internal energy (E) of ions undergoing fragmentation by eq 2.[23] For two competing processes, such as the partitioning

$$\ln k = \ln \nu - (s-1)E_0/E(1 + \tfrac{1}{2}E_0/E + \ldots) \qquad (2)$$

of a proton between two interacting bases of similar PA, in the metastable window, it can be assumed that $E'_0/E \simeq E''_0/E \simeq 1$. Therefore eq 3 can be derived, where A is a constant for the investigated process. A similar expression has been obtained from

$$\ln k_1/\ln k_2 = \ln \nu_1/\ln \nu_2 + A(s-1)(\Delta E_0/E) \qquad (3)$$

the Arrhenius dependence of the rate constants of the competitive breakdown of proton-bound species.[16]

Assuming that these processes are characterized by similar entropy changes (similar frequency factors) and small reverse activation energies, it can be concluded that the difference in the critical energies (ΔE_0) for the two competing processes can be considered equivalent to the difference in proton affinities (ΔPA) of the two interacting species, and the ratio of ion abundances is equal to the ratio of the rate constants, which in turn can be related to proton affinity differences by eq 4.[16] In the case of

$$\ln (k_1/k_2) = [(s-1)/E]\Delta PA \qquad (4)$$

the unimolecular dissociations given in eqs 1a and 1b, eq 4 can be written in the form

$$\ln (k_N/k_a) = [(s-1)/E](PA_N - PA_a) \qquad (5)$$

where k_N and k_a are the kinetic constants for the formation of protonated nucleoside (or nucleobase) and reference amine, respectively, and PA_N and PA_a are the correspondent proton affinities. If the unimolecular dissociations of proton-bound heterodimers formed by a given nucleoside (or nucleobase) with two different amines are compared, the unknown proton affinity can be related, on the basis of eqs 6 and 7, to the relative abundances

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Table I. (v^+) FAB Spectra of Amine Clusters[a]

dN (or B)/amine	$[B+H]^+$	$[dN+H]^+$	$[B+a+H]^+$ or $[dN+a+H]^+$
1. dA/TPA	100	25	5
2. dC/TPA	100	17	10
3. dG/TPA	100	38	7
4. dT/PIP	100	22	11
5. Ade/PYR	100		20
6. Cyt/PYR	100		20
7. Gua/PYR	58		100
8. Thy/ANI	100		30

[a] Partial (v^+) FAB spectra of some of deoxynucleosides (dN) or nucleobases (B) with tripropylamine (TPA), piperidine (PIP), pyrrolidine (PYR), and aniline (ANI). *m*-Nitrobenzyl alcohol (entries 1-5) and thioglycerol (entries 6-8) have been used as matrices.

of the protonated species formed in the breakdown of the clusters and to the known PA's of the reference compounds. Equation

$$\ln [(k_N/k_{a1})/(k_N/k_{a2})] = (PA_N - PA_{a1})/(PA_N - PA_{a2}) \quad (6)$$

$$PA_N = \frac{[\ln (k_N/k_{a1})]PA_{a2} - [\ln (k_N/k_{a2})]PA_{a1}}{\ln (k_N/k_{a1}) - \ln (k_N/k_{a2})} \quad (7)$$

7 holds for the dissociation of proton-bound dimers formed by a given species with two different reference compounds of similar structure and PA. Under this condition, in fact, it can be assumed that the internal energy and the number of effective oscillators of the reactant ions are similar.

The applicability of the methodology and of eq 7 has been verified by measuring the PA's of the four DNA nucleobases. In this case values (kcal/mol) were determined[24] for Thy (208.8), Ade (223.5), and Cyt (223.8) and estimated[24] for Gua (~223). These data, however, do not allow a distinction to be made among the relative basicity properties of the last three nucleobases, whose PA differences are within the limit of the experimental error.

A high yield or protonated dimers is a prerequisite for the application of the FAB-bracketing method. In this approach, in fact, the charged clusters are allowed to react either spontaneously or after collisional activation in the second field free region of a B-E mass spectrometer. The MIKE spectra[25] thus obtained show product ions whose relative abundances can be up to three orders of magnitude lower than that of the parent reacting species. In the experiments discussed below, the best results were obtained by using saturated solutions of nucleobases (B) or deoxynucleosides (dN) and the appropriate amine (a) in acidic matrices such as 1-mercapto-2,3-dihydroxypropane (THIOGLY) and 3-nitrobenzyl alcohol (MNBA). The solutions thus obtained afforded, after bombardment with 9.5-keV Xenon atoms, long-lasting positive (v^+) FAB spectra characterized by very high total ion current and by the presence of abundant protonated clusters (Table I). Pyrrolidine (PYR, PA = 225.2 kcal/mol) and piperidine (PIP, PA = 226.4 kcal/mol) were chosen as references for Ade, Cyt, and Gua, whereas aniline (ANI, PA = 209.5 kcal/mol) and 3-bromoaniline (BAN, PA = 208.1 kcal/mol) were used for Thy, because their known PA's[24] are in the range of those reported for the nucleobases.

The MIKE spectra of the clusters $[B+PYR+H]^+$ (Table II, entries 1, 3, and 5) and $[B+PIP+H]^+$ (entries 2, 4, and 6) are characterized by the presence of two product ions due to the formation of $[B+H]^+$, $[PYR+H]^+$, and $[PIP+H]^+$ species, respectively. The k_N/k_a ratios (eq 7) were determined from the relative abundances of the appropriate product ions, corrected for the discrimination effect of the electron multiplier,[26] with a standard deviation in the range of 5%, as expected from a MIKE experiment. PA values of 224.2, 225.9, and 227.4 kcal/mol were calculated by means of eq 7 for adenine, cytidine, and guanine,

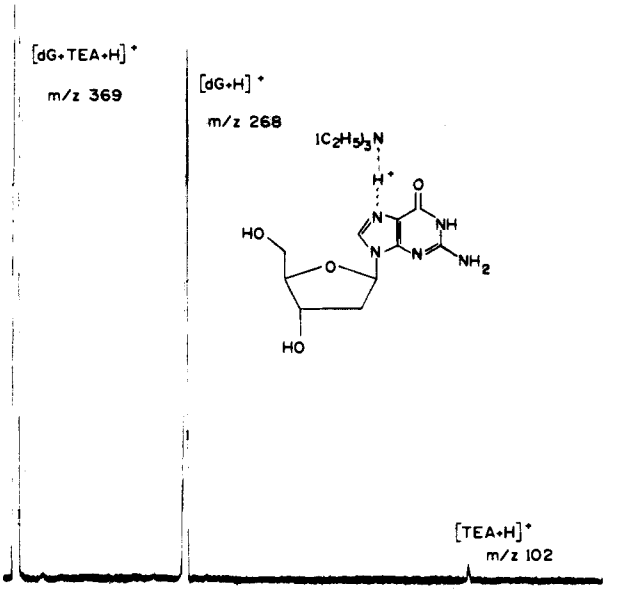

Figure 1. MIKE spectrum of the proton-bound dimer formed by FAB (thioglycerol) from deoxyguanosine (dG) and triethylamine (TEA).

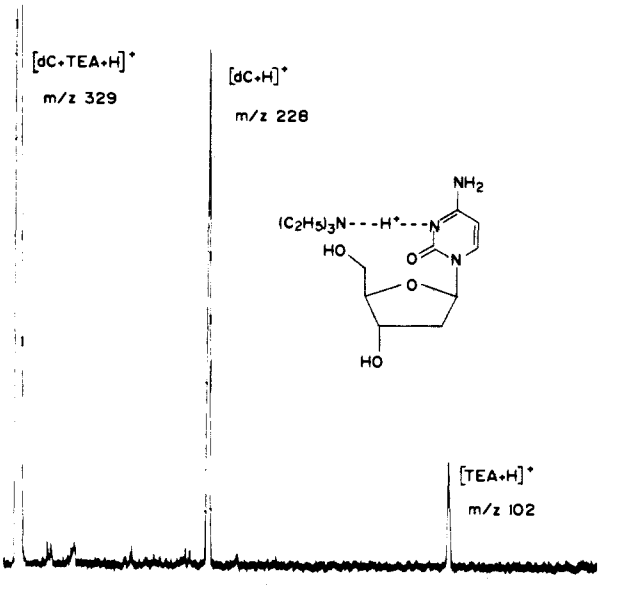

Figure 2. MIKE spectrum of the proton-bound dimer formed by FAB (thioglycerol) from deoxycytidine (dC) and triethylamine (TEA).

respectively. Similarly, 209.0 kcal/mol was assigned to the proton affinity of thymine, from the data provided by the unimolecular dissociations of the clusters $[Thy+ANI+H]^+$ and $[Thy+BAN+H]^+$ (entries 7 and 8, Table II). Standard deviations in the range of ±0.1 kcal/mol were calculated from the partial derivative of eq 7 by means of the experimentally determined standard deviations of the k_N/k_a ratios. These results confirm that adenine, cytosine, and guanine have very similar PA's, quite different from that of thymine. The values thus determined are close to those previously obtained by high-pressure mass spectrometric measurements;[13,14,23] however, a clear differentiation is now possible. The basicity order of the four DNA nucleobases in the gas-phase basicity is Gua > Cyt > Ade ≫ Thy. Moreover, the unknown PA of Gua has been confidently assigned.

A first discrimination among the four deoxynucleosides present in natural DNA, in relation to their proton affinity scale, simply comes from the MIKE spectra of the protonated heterocomplexes reported in Table III. The PA of dT, in fact (entries 7 and 8), can be determined by bracketing with secondary amines such as pyrrolidine and piperidine, whereas the most basic species requires the use of triethylamine (TEA, 232.3 kcal/mol) and tripropylamine (TPA, 234.0 kcal/mol).[23] Deoxythimidine, therefore, is the least basic nucleoside among those present in DNA, and its

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Table II. MIKE Spectra of Nucleobases–Amine Clusters[a]

base (B)	% rel [B+H]$^+$	[PYR+H]$^+$	[PIP+H]$^+$	[ANI+H]$^+$	[BAN+H]$^+$
1. Adenine	48.9	51.1			
2. Adenine	25.3		74.7		
3. Cytosine	83.1	16.9			
4. Cytosine	41.9		58.1		
5. Guanine	91.6	8.4			
6. Guanine	76.3		23.7		
7. Thymine	32.2			67.8	
8. Thymine	87.4				12.6

[a] Relative percentage of the daughter ions (five scans average) of the proton-bound dimers of nucleobases with pyrrolidine (PYR), piperidine (PIP), aniline (ANI), and *m*-bromoaniline (BAN).

Table III. MIKE Spectra of Deoxynucleosides–Amine Clusters[a]

dN	% rel [dN+H]$^+$	[TEA+H]$^+$	[TPA+H]$^+$	[PYR+H]$^+$	[PIP+H]$^+$
1. dA	90.9	9.1			
2. dA	52.9		47.1		
3. dC	90.7	9.3			
4. dC	28.7		71.3		
5. dG	97.2	2.8			
6. dG	75.6		24.4		
7. dT	50.0			50.0	
8. dT	30.0				70.0

[a] Relative percentage of the daughter ions (five scans average) of the proton-bound dimers of deoxynucleosides with triethylamine (TEA), tripropylamine (TPA), pyrrolidine (PYR), and piperidine (PIP).

proton affinity should be close to that of the purine nucleobases. On the other hand, the basicity properties of dA, dC, and dG should be very similar, as suggested by the unimolecular dissociations of their proton-bound dimers (Figures 1–3 and Table III). Moreover, the PA of a given nucleoside is higher than that of the corresponding purine or pyrimidine base; therefore, estimations based on the proton affinity values of the nucleobases are incorrect.[24]

The application of eq 7, using the data reported in Table III, provides the PA values 234.4, 233.6, 233.2, and 224.9 kcal/mol for dG, dA, dC, and dT, respectively, whose standard deviations, calculated as previously described, are in the range of ±0.1–0.2 kcal/mol. Although the calculated values might be affected by the approximations made in deriving eq 7, the experimental results obtained from the unimolecular dissociations of the examined proton-bound heterocomplexes (Table III) clearly indicate that the four DNA nucleosides follow, in the absence of solvent effects, the proton affinity order dG >dA ≅ dC ≫ dT.

Significant deviations in the k_N/k_a ratios (eq 3) were not observed when THIOGLY was used instead of MNBA in the formation of the protonated clusters. Actually, the choice of the matrix affects only the quality of the spectra of the secondary ions and the signal-to-noise ratio of the MIKE measurements which is correlated to the different ion current of the parent species produced from the two matrices. A deep insight into the factors that influence the formation and the structure of the reacting proton-bound pairs, and thus the evaluation of the proton affinities, has been obtained by following the unimolecular dissociations of [dG+TPA+H]$^+$ produced by FAB under extremely different experimental conditions (Table IV). Water solutions of dG and tripropylamine, initially frozen in liquid nitrogen, were exposed to atom bombardment. The experiment was repeated with 0.01 N aqueous HCl/MNBA solutions of the same reactants. The MIKE spectra of the proton-bound heterocomplexes thus formed do not differ and do not show significant differences with those obtained from the same reactant formed from the other matrices. Hydrogen bonding in solution is favored in apolar solvents; water, in fact, tends to solvate fully either each solute molecule or stacked dN pairs.[27] Moreover, in strong acid medium (0.01 N HCl) it can be assumed that the equlibria given in eqs 8 and 9 are shifted toward the formation of the corresponding conjugated acids. The

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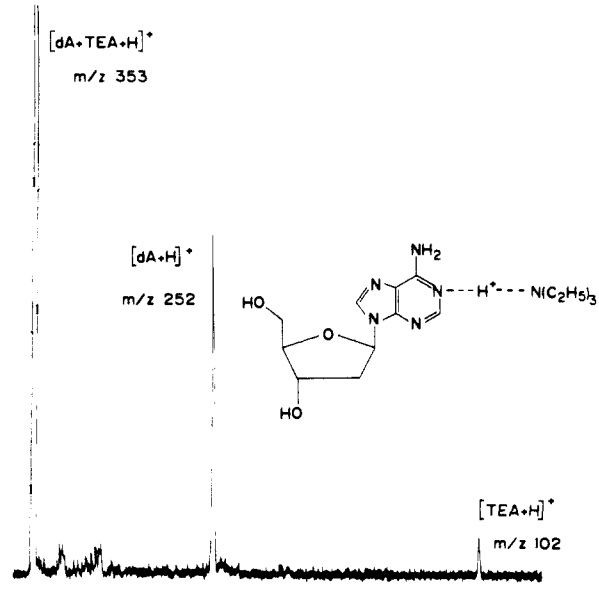

Figure 3. MIKE spectrum of the proton-bound dimer formed by FAB (thioglycerol) from deoxyadenosine (dA) and triethylamine (TEA).

Table IV. MIKE Spectra of [dG + TPA + H]$^+$ from Different Matrices[a]

matrix	% rel [dG+H]$^+$	[TPA+H]$^+$
1. MNBA	75.6	24.4
2. MNBA/0.01 N HCl	76.6	23.4
3. THIOGLY	73.9	26.1
4. H_2O	62.7	37.3

[a] Relative percentage of the daughter ions. MNBA (*m*-nitrobenzyl alcohol), THIOGLY (1-mercapto-2,3-dididroxypropane).

structure similarity of the clusters formed under such different conditions, as suggested by their unimolecular dissociations in the

$$dG + H^+ \rightleftharpoons (dG+H)^+ \quad (8)$$

$$TPA + H^+ \rightleftharpoons (TPA+H)^+ \quad (9)$$

gas phase (Table IV), points out that an equilibrium between the proton-bound complexes and the interacting monomers should be reached after the initial sputtering event. This observation is particularly valid when the protonated monomers are preformed on the surface exposed to particle bombardment.

The PA values reported above indicate that the protonation site of a given nucleoside is located on the nucleobase moiety. The PA of thymidine is closer to that of unsaturated heterocyclic amides such as 1-methyl-2-pyridone (220.2 kcal/mol),[24] thus suggesting that the amide group of the pyrimidine is preferentially protonated. The similarity of the PA values of the more basic nucleosides with that of 1-methylimidazole (228.9 kcal/mol)[24] could suggest the protonation of the amidine functional groups of the nucleobases. Calculations performed on the nucleobases Thy, Cyt, Ade, and Gua, using fully optimized geometries with an extended basis set,[28] have shown that their most stable con-

jugated acids correspond to O_4-H, N_3-H, N_1-H, and N_7-H protonated species, respectively. The same protonation sites were experimentally determined for the corresponding deoxynucleosides in solution[29] and in the solid state.[30] If the examined clusters are formed under equilibrium conditions, by recombination in the selvedge,[3] it can be assumed that the same sites are involved in the formation of the proton-bound dimers. Nevertheless, the population of different tautomers does not alter the main observation related to the basicity order of the examined species.

The enhanced basicity of the deoxynucleosides over the corresponding bases was explained to be due to the formation of intramolecular hydrogen bonds among the base and the sugar moieties.[14] An alternative explanation for the observed phenomenon can consider the electron-donating effect exerted by the deoxyribose on the linked purine or pyrimidine rings. The inversion of the basicity order of dA and dC, which indeed exhibit very similar PA's, with respect to their corresponding nucleobases Ade and Cyt, might be due to different effects exerted by the deoxyribose unit. This borderline situation accounts for the observed slight preference in the formation of $[dA+H]^+$ in the dissociation of $[dA+dC+H]^+$ species.[11] In the latter case, however, it must be considered that mixtures of multiple hydrogen-bonded pairs can be formed,[13] which affect the unimolecular dissociation of the cluster, and thus, an accurate estimation of the relative proton affinities of the two interacting components.

Conclusion

Fast atom bombardment methodology can be used to form protonated heterocomplexes, whose gas-phase unimolecular dissociations can provide a probe of their relative proton affinities. This kinetic approach has given, for the first time, stratightforward information on the relative basicity scale of DNA nucleosides and related nucleobases in the absence of solvent effect. The experimental PA order dG > dA = dC ≫ dT differs from that of the corresponding nucleobases, Gua > Cyt > Ade ≫ Thy, evaluated under the same conditions. The uniqueness of the applied methodology lies in the fact that a clear distinction has been made among the gas-phase basicity of the most basic nucleosides and corresponding nucleobases, which possess very similar proton affinity properties.

Experimental Section

Deoxynucleosides, pyrimidines, and purines were purchased from Fluka; amines and matrices were purchased from Aldrich. Saturated solutions (1-2 μL) of nucleic acid materials and the appropriate amines were deposited on the target of the FAB probe. When H_2O was used as the matrix, the corresponding solutions were frozen by dipping the covered target into liquid nitrogen. Mass spectra were obtained on a Vacuum Generators (VG) ZAB-2F instrument operated at an accelerating potential of 8 kV by using the M-SCAN steerable FAB gun. A neutral Xe beam of 9.5 keV energy and a neutral current of ca. 10 μA were employed. The spectra were recorded at 1000 resolution by scanning the magnetic field. The MIKE spectra were recorded by scanning down the electrostatic sector potential. The standard deviations on the k_N/k_a values were determined from five independent measurements, and the error propagation on the calculated PA's was computed from the squared partial derivative of eq 7.

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Metal-Assisted Hydroformylation on a SiO_2-Attached Rh Dimer. In Situ EXAFS and FT-IR Observations of the Dynamic Behaviors of the Dimer Site

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Abstract: *trans*-$[Rh(C_5Me_5)(CH_3)]_2(\mu\text{-}CH_2)_2$ was supported on the SiO_2 surface by the reaction with OH groups of SiO_2 at 313 K, followed by evacuation at 373 K. In this attaching reaction, the Rh dimer complexes were bound to the SiO_2 surface through Rh-O(surface) bonds, losing one CH_3 ligand and one C_5Me_5 ligand per Rh dimer. The attached Rh dimers were found to be more active and selective than a conventionally prepared Rh/SiO_2 catalyst. The structure change of the Rh dimer sites in each reaction step for catalytic hydroformylation was followed by means of in situ FT-IR and in situ EXAFS techniques. The Rh-Rh bond in the attached Rh dimers (Rh-Rh = 0.262 nm) was cleaved by CO adsorption to form monomer pairs $[Rh(C_2H_5)(CO)_2(O\text{-}Si) + Rh(C_5Me_5)(O\text{-}Si)]$. Heating the monomer pairs to 423 K under vacuum resulted in CO insertion, with new peaks exhibited at 1710 and 1394 cm^{-1} due to the acyl ligand. The insertion was promoted by rebonding of the two adjacent Rh atoms observed at 0.270 nm. The Rh-acyl dimers were reversibly converted to the previous monomer pairs without Rh-Rh bonding by CO admission. These behaviors of Rh dimers on SiO_2 are entirely different from usual Rh monomer chemistry. A new metal-assisted reaction mechanism is described.

Introduction

Organometallic dimers and clusters have been widely studied in order to prepare dispersed metal sites with well-defined compositions on inorganic supports and to elucidate catalytic reaction mechanisms on a molecular level.[1-3] Irrespective of definite structures and compositions of starting metal clusters, the relationship between structure and catalytic performance is often poorly defined and catalytic sites remain unidentified because we

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