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Intrinsic acidity and redox properties of the adenine radical cation

C. Thomas Hwang, Chris L. Stumpf, Ying-Qing Yu, Hilkka I. Kenttämaa*

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393, USA

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Abstract

The intrinsic chemical properties of the gaseous adenine radical cation were examined by using dual cell Fourier transform ion cyclotron resonance mass spectrometry. The adiabatic recombination energy of the radical cation (ionization energy of neutral adenine) was found by bracketing experiments to be 8.55 ± 0.1 eV (at 298 K; earlier literature values range from 8.3 to 8.9 eV). Based on this value, the heat of formation (ΔH_f^{298}) of the adenine radical cation is estimated to be 246 ± 3 kcal/mol. The acidity (ΔH_{acid}^{298}) of the adenine radical cation was bracketed to be 221 ± 2 kcal/mol. These thermochemical values suggest that the adenine radical cation reacts with neutral guanine by electron abstraction or proton transfer, with neutral cytosine by proton transfer, and via neither pathway with neutral thymine, molecular water or a sugar moiety of DNA (modeled by tetrahydrofuran). Experimental examination of the gas-phase reactivity of the adenine radical cation revealed a slow deuterium atom abstraction from perdeuterated tetrahydrofuran. Hence, in the absence of a nearby guanine or cytosine, the adenine radical cation may be able to abstract a hydrogen atom from a sugar moiety of DNA. (Int J Mass Spectrom 182/183 (1999) 253–259) © 1999 Elsevier Science B.V.

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1. Introduction

Cleavage of DNA induced by UV light is thought to occur by direct and indirect pathways [1]. The indirect pathway is initiated by ionization of solution components (usually water) contained within the cell that ultimately abstract a hydrogen from the deoxyribose moiety of DNA [1]. This mechanism has received most attention thus far. The direct cleavage pathway [2] is initiated by ionization of one of the DNA bases to generate a base radical cation within the DNA. The charge is thought to migrate [3–10] some distance along the DNA helix from base to base. Charge transfer is eventually interrupted [3], for example, by proton transfer within one of the hydrogen bonded base pairs (A–T or G–C), thus separating the charge from the radical site. The resulting radical is believed to abstract a hydrogen atom from a nearby deoxyribose (C1′ position), which leads to DNA cleavage via a poorly understood fragmentation process [11].

In spite of numerous experimental studies of DNA base radical cations in solution and in biological

* Corresponding author.

Dedicated to the memory of Ben Freiser to commemorate his many seminal contributions to mass spectrometry and gas phase ion chemistry.

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systems [1–10,12], the current understanding of the mechanism of the direct DNA cleavage process is limited. For example, the relative likelihood for charge migration to stop and proton transfer to take place at a specific base pair is not known. Further, the importance of various other possible processes is unknown, i.e. reactions of the nucleobase radical cations with water or the sugar moiety of DNA. The difficulty in being able to predict the reactivity of the nucleobase radical cations arises partially from *the nearly complete absence of thermochemical data* relevant to the reactions in question. For example, the recombination energies and acidities of the isolated base radical cations are poorly known [13].

Mass spectrometry is a powerful experimental tool for the determination of thermochemical values for ions and neutral compounds [13,14]. We report here an examination of the intrinsic (solvent-free) reactivity of the adenine radical cation and the determination of its recombination energy and gas-phase acidity by using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR).

2. Experimental

The experiments were carried out in a dual cell Extrel model 2001 Fourier transform ion cyclotron resonance mass spectrometer [15,16]. The instrument contains two identical 2 in. cubic cells separated by a common wall, the conductance limit. The cells are placed within a 3.0 Tesla solenoid superconducting magnet operated at 2.6–2.8 Tesla. The cell most often used for detection is in the most homogeneous part of the magnetic field. The cells are differentially pumped with two Balzers turbomolecular pumps (330 L/s), each backed with an Alcatel 2012 mechanical pump. The nominal base pressure in each cell is less than 1×10^{-9} Torr, as measured with an ionization gauge on each side of the dual cell. A Sun IPX data station running Odyssey software version 3.0, or a Nicolet 1280 computer system, was used for data acquisition and processing.

Each sample was introduced into one side of the dual cell through a heated solids probe, a Varian leak valve, a set of pulsed valves [17], or a batch inlet system equipped with a variable leak valve. Adenine was introduced at a nominal pressure of approximately 4×10^{-8} Torr by using the heated solids probe ($T \sim 140$ °C). The various other reagents were introduced into the other side of the dual cell at a nominal pressure of 1×10^{-7} Torr.

Primary ions were generated by electron ionization of the appropriate neutral precursors. The ionization conditions were optimized by varying the filament current (~8 μA), ionization time (30–100 ms), and electron energy (18–85 eV). Ions were trapped by applying a +2 V potential to the three cell plates perpendicular to the magnetic field lines (trapping plates). After generation in one cell, ions were transferred into the other cell through a 2 mm diameter hole in the trapping plate common to the two cells (conductance limit) by temporarily grounding this plate (~160 μs). Before the transfer event, ions in the receiving cell were removed by applying a negative potential (−10 V) to the remote trapping plate of this cell (5 ms). As the ions reached the receiving cell, they were cooled (usually for 200–500 ms) by collisions with argon introduced into the cell through pulsed valves at a peak pressure of 1×10^{-5} Torr. Cooling the transferred ions ensured that only exothermic or thermoneutral reactions can take place [18].

Stored-waveform inverse Fourier transform (SWIFT) [19] excitation pulses were applied to the excitation plates of the cell to eject unwanted ions from the cell (Extrel FTMS SWIFT Module). The SWIFT ejection pulses were designed so that excitation of the ions of interest was kept to a minimum. The isolated ion was allowed to react with a neutral reagent for various time durations until 90%–95% of the ions had reacted. To eliminate product ions arising from minor impurity ions still left in the cell after ion isolation, a background subtraction procedure was followed. The background spectrum was produced by removing the isolated ion and acquiring a spectrum for the same reaction time as was used to produce the corresponding reaction spectrum.

Ion detection was accomplished by using a SWIFT [19] excitation pulse to excite ions (m/z 17–800) to a

Table 1
Results obtained for the reactions of the adenine radical cation (m/z 135) with various neutral reagents

Neutral reagent (MW)[a]	Reaction efficiency, k/k_{coll}	Primary products (m/z)	Branching ratios
Dimethyl disulfide (94)	NA[b]	$C_2H_6S_2^{+\cdot}$ (94)	1.0
Anisole (108)	1.26	$C_7H_8O^{+\cdot}$ (108)	0.7
Trimethyl phosphite (124)	0.99	$(CH_3O)_3P^{+\cdot}$ (124)	0.8
		$(CH_3O)_3PH^+$ (125)	0.2
Ethyl methyl sulfide (76)	low	$C_3H_8S^{+\cdot}$ (76)	1.0
Iodobenzene (204)	0.00[c]	None	···
Isobutylamine (73)	~0.00[c]	$C_4H_9NH_3^+$ (74)	1.0
N,*N*-Dimethylacetamide (87)	0.00[c]	None	···
Tropone (106)	NA[b]	[Adduct–NH_3] (224)	0.4
		[Adduct] (241)	0.6
3-Picoline (93)	0.41	$C_6H_7NH^+$ (94)	1.0
Pyridine (79)	0.15	$C_5H_5NH^+$ (80)	1.0
Acetone (58)	0.00[c]	None	···
Triethyl phosphate (182)	0.00[c]	None	···
Trimethyl phosphate (140)	0.00[c]	None	···
Isopropyl acetate (102)	0.00[c]	None	···
Perdeuterated tetrahydrofuran (80)	~0.004	$C_5H_5N_5D^+$ (137)	1.0

[a] The proton affinities and ionization energies are listed in Tables 2 and 3.
[b] Not applicable; the rate constant cannot be determined because of competing reaction involving self-protonation between the adenine radical cation and neutral adenine diffusing from the other cell.
[c] Reactions with efficiencies <0.001 cannot be detected under these conditions.

final cyclotron radius of 0.5 cm. The time domain signal transients, recorded as 32 k data points at a digitizer rate of 5.3 MHz, were subjected to one zero fill before Fourier transformation.

The reaction rate constants (k in cm^3 $molecule^{-1}$ s^{-1}), were determined from the decay of the reactant ion abundance (normalized to the total ion current) as a function of time. The concentration (pressure) of the neutral reagent was obtained by calibrating the ion gauges for their sensitivity toward the neutral reagent and for the pressure gradient between the ion gauge and the dual cell. The latter correction factor was obtained by measuring the rates of several exothermic proton and electron transfer reactions expected to occur at collision rate. The collision rate constants (k_{coll}) were calculated by using a parameterized trajectory theory [20]. Reaction efficiencies are given as the ratio of the reaction rate constant to the collision rate constant (k/k_{coll}). The precision of the rate measurements is better than ±10% with an estimated accuracy of ±50%. The primary reaction products were identified based on their constant branching ratios at short reaction times.

All reagents were purchased from commercial sources and used without further purification. The identities and purities of all reagents were verified by mass spectrometry and gas chromatography.

3. Results and discussion

Gas-phase reactions of the isolated adenine radical cation were examined as a function of time with several neutral reagents. The reaction products, their branching ratios, and the reaction efficiencies are given in Table 1. The most commonly observed reactions were proton and electron transfer. However, tetrahydrofuran was found to react by another pathway (slow hydrogen atom transfer).

The ability to predict the occurrence of proton and electron transfer reactions requires knowledge of the relevant thermochemical data, i.e. adiabatic recombi-

nation (ionization) energies for electron transfer reactions, and proton affinities (or ΔH_{acid}) for proton transfer reactions. However, these values were either not available or not well known for the adenine radical cation [13]. Hence, mass spectrometry was employed to determine these values.

A well-established method used to determine thermochemical values by mass spectrometry is to measure an equilibrium constant for a nearly thermoneutral reaction [21]. However, when a chemical equilibrium cannot be established because of competing reactions and/or the formation of a radical or other unstable or highly reactive molecule as one of the products, the bracketing method is an alternative [22]. In this study, the bracketing method was employed to quantify the recombination energy and gas-phase acidity of the adenine radical cation and the ionization energy of neutral adenine. The bracketing method involves the examination of the reactions of the species of interest, e.g. the adenine radical cation, with reference compounds with known thermochemical properties. Assuming that entropy changes are small, the efficiency (k/k_{coll}) of the gas-phase reaction is controlled by enthalpy [14,22]. Hence, the transition from exothermic to endothermic processes can be identified by examining the appearance or absence of specific product ions. The accuracy of the values determined by these experiments is limited by the fact that transition from fast reactions (exothermic) to immeasurably slow reactions (endothermic) is typically gradual.

3.1. Determination of the recombination energy of the adenine radical cation

Theoretical [23] and experimental studies [13,24,25] have been carried out by others to obtain an estimate for the ionization energy of adenine. The highest level of theory employed thus far (MP2/6-31+G(d)//UHF/6-31G(d)) yielded 8.18 and 8.58 eV for the adiabatic and vertical ionization energies, respectively [23]. All experimentally determined adiabatic ionization energy values are greater than the theoretical prediction, ranging from 8.3 up to 8.9 eV. The reported experimental vertical ionization energies range from 8.4 up to 8.5 eV. Hence, there is great ambiguity concerning the ionization energy of adenine. The recombination energy of the adenine radical cation has not been measured before.

Table 2
Bracketing the adiabatic recombination energy (RE) of the radical cation of adenine (m/z 135) and the ionization energy (IE) of neutral adenine: adenine$]^{+\cdot}$ + reagent $\rightleftharpoons$ adenine + reagent$]^{+\cdot}$

Reagent (MW)	Ionization energy[a] (eV)	Forward reaction[b] (RE)	Reverse reaction[b] (IE)
Dimethyl disulfide (94)	8.1 ± 0.2[c]	+	−
Anisole (108)	8.20 ± 0.05	+	−
Trimethyl phosphite (124)	8.4	+	−
Ethyl methyl sulfide (76)	8.55 ± 0.01	+	+
Iodobenzene (204)	8.72 ± 0.04	−	+
Tropone (106)	8.88 ± 0.05	−	+

[a] Values taken from [13].
[b] A negative value (−) indicates that no electron transfer was observed, while a positive value (+) indicates that electron transfer was observed.
[c] Values taken from [18].

The adiabatic recombination energy (RE) of the adenine radical cation was determined by forward (RE) and reverse [ionization energy (IE) of adenine] bracketing experiments (Table 2; the thermochemical values obtained are adiabatic since the reactions occur on a time scale long enough for a geometry change). Examination of the reactions of ethyl methyl sulfide (8.55 ± 0.1 eV) were especially informative. Both the forward and reverse electron transfer reactions were observed for this reagent, which suggests that the recombination energy of the adenine radical cation (and hence, the adiabatic IE of adenine) must be close to 8.55 eV (Table 2). The adenine radical cation reacts by electron transfer with neutral reagents with an IE lower than 8.55 eV (these reagents, when ionized, do not abstract an electron from adenine) but not with reagents with IE at or above 8.72 eV (the reverse reactions occur readily). Hence, the adiabatic recombination energy of the adenine radical cation (and the adiabatic IE of adenine) is concluded to be 8.55 ± 0.1 eV. This value falls in the middle of the experimental

values reported earlier in the literature for the adiabatic ionization energy of adenine (8.26–8.91 eV) [13] and is greater than the theoretically predicted value (8.18 eV) [23]. Based on an adiabatic recombination energy of 8.55 eV, the heat of formation (ΔH_f^{298}) of the adenine radical cation is estimated to be 246 ± 3 kcal/mol (ΔH_f^{298} of neutral adenine [13] is 49 ± 2 kcal/mol). The fact that the adiabatic ionization and recombination energies measured here are in good agreement implies that adenine does not rearrange (change connectivity) upon ionization [26].

The adiabatic ionization energies of guanine, thymine, and cytosine have been reported to be 7.77, 8.87, and 8.68 eV, respectively [23,25]. An earlier computational study predicts that base pairing has an insignificant effect on the ionization energies of adenine and thymine and about 0.5 eV on those of cytosine and guanine [27]. Hence, the adenine radical cation is expected to react with guanine by electron abstraction because this process is exothermic. Electron abstraction from the other DNA bases would be endothermic and thus is not likely to occur.

3.2. Determination of the gas-phase acidity of the adenine radical cation

The gas-phase acidity of the adenine radical cation (i.e. the proton affinity of the (adenine–H) radical) has not been measured, in spite of its obvious importance in aiding the understanding of the direct DNA cleavage mechanism [1–3,28]. Hence, the gas-phase acidity was experimentally determined by bracketing experiments employing a series of reference bases with known proton affinities (Table 3). The adenine radical cation does not transfer a proton to acetone, isopropyl acetate, trimethyl phosphate, *N*,*N*-dimethyl acetamide, triethyl phosphate or tropone. Hence, the proton affinity of tropone (220.1 kcal/mol) serves to set the lower limit for the proton affinity of the (adenine–H) radical at 220 kcal/mol. Proton transfer was observed to occur to trimethyl phosphite (PA = 222.2 kcal/mol) and to two reference bases with proton affinities greater than that of trimethyl phosphite, namely pyridine and 3-picoline. This sets the upper limit for the proton affinity of the (adenine–H) radical at 222 kcal/mol. Slow proton transfer (indicating a nearly thermoneutral reaction) was observed for isobutylamine (PA = 221.0 kcal/mol). Therefore, the proton affinity of the (adenine–H) radical (or gas-phase acidity of the adenine radical cation) is concluded to be 221 ± 2 kcal/mol.

Table 3
Proton transfer from the adenine radical cation to various neutral reference bases: adenine$]^{+\cdot}$ + base → (adenine − H)$^{\cdot}$ + base-H^{+}

Neutral reagent (MW)	Proton affinity (kcal/mol)[a]	Proton transfer[b]	Reaction efficiency,[c] k/k_{coll}
Acetone (58)	196.7	−	NA[d]
d-Tetrahydrofuran (80)	198.8	−	NA
Isopropyl acetate (102)	~200.6 [e]	−	NA
Trimethyl phosphate (140)	212.0	−	NA
N,*N*-Dimethylacetamide (87)	216.2	−	NA
Triethyl phosphate (182)	217.0	−	NA
Isobutylamine (73)	218.8	+[f]	[g]
Tropone (106)	219.0	−	NA
Trimethyl phosphite (124)	220.6	+	0.99
Pyridine (79)	220.8	+	0.15
3-Picoline (93)	224.1	+	0.41

[a] Values taken from [13].
[b] A negative value (−) indicates that proton transfer was not observed, while a positive value (+) indicates that proton transfer was observed.
[c] Efficiency of proton transfer ($k_{\text{proton transfer}}/k_{coll}$)
[d] Not applicable
[e] Value is estimated to be equivalent to the proton affinity of *n*-propyl acetate.
[f] Reaction is accompanied by a competing reaction involving self-protonation between the adenine radical cation and neutral adenine diffusing from the other cell.
[g] Rate constant cannot be determined (see footnote e).

The gas-phase acidity value obtained for the adenine radical cation indicates that this species is more acidic than protonated adenine (according to literature, the PA of adenine [13] is 225.3 kcal/mol). The proton affinity of adenine, thymine, guanine, and cytosine have been reported to be 225.3, 208.8, ~223, and 223.8 kcal/mol, respectively [13,29]. Based on the above information, the adenine radical cation is expected to readily protonate neutral guanine, cytosine, and adenine since these processes would be

exothermic. Proton transfer between the adenine radical cation and neutral thymine is not expected to occur due to the endothermicity of the reaction. Finally, it is commonly thought [3,30] that the nucleobase radical cations are acidic enough to transfer a proton to water. However, the results obtained in this study demonstrate that proton transfer from the adenine radical cation to molecular water is highly endothermic (52 kcal/mol; acidity of adenine is 219 ± 2 kcal/mol; proton affinity [13] of water is 166.5 kcal/mol).

3.3. Reaction of the adenine radical cation with perdeuterated tetrahydrofuran

The measured recombination energy of the adenine radical cation, combined with the literature value for the proton affinity of adenine (and IE of hydrogen atom), gives 109 kcal/mol as the hydrogen atom affinity of the adenine radical cation. This value is greater than the homolytic bond dissociation energies of many C–H bonds. However, as Table 1 demonstrates, the adenine radical cation does not readily abstract hydrogen atoms from organic substrates. These reactions are likely to be hindered by significant energy barriers [31,32].

In order to probe whether the adenine radical cation is able to abstract a hydrogen atom from the sugar unit of DNA, reactions of tetrahydrofuran were examined. The ionization energy of tetrahydrofuran is significantly greater (9.41 eV) than the recombination energy of the adenine radical cation, which explains the absence of electron transfer between these molecules (Table 1). Similarly, proton transfer from the adenine radical cation to tetrahydrofuran (PA = 198.8 kcal/mol) is endothermic and does not take place. Instead, the adenine radical cation undergoes a very slow deuterium atom abstraction from neutral perdeuterated tetrahydrofuran (Table 1). This observation suggests that the adenine radical cation may be able to induce DNA strand cleavages via hydrogen abstraction from the sugar moiety, provided that it cannot undergo the kinetically more favorable electron abstraction or proton transfer reactions with other nearby molecules.

4. Conclusions

The adenine radical cation is a strong Brönsted acid and a strong oxidant, and preferentially reacts with organic molecules by electron abstraction or proton transfer. The adiabatic recombination energy of the adenine radical cation was found to be 8.55 ± 0.1 eV. This value falls in the middle of the previously reported experimental adiabatic ionization energy values of neutral adenine (8.26–8.91 eV) but is greater than the calculated literature value (8.18 eV) [13,22,24]. Based on a recombination energy of 8.55 ± 0.1 eV, the heat of formation (ΔH^{298}) of the adenine radical cation is estimated to be 246 ± 3 kcal/mol. The equivalence of the measured recombination and ionization energies indicate that the connectivity of the neutral and ionized adenine are the same, i.e. adenine does not rearrange upon ionization. The acidity of the adenine radical cation (221 ± 2 kcal/mol) was found to be significantly greater than that of protonated adenine.

Based on the results obtained in this study and the earlier computational prediction that base pairing has an insignificant effect on the ionization energies of adenine and thymine and a relatively small effect (~0.5 eV) on those of cytosine and guanine [27], one concludes that an adenine radical cation formed in a DNA molecule upon UV irradiation is most likely to react with nearby molecules by proton or electron transfer. Specifically, the adenine radical cation is expected to react with neutral guanine and adenine either by electron abstraction or proton transfer, with neutral cytosine by proton transfer, and not at all with neutral thymine or molecular water (assuming that the previously reported [13,29] adiabatic ionization energies and proton affinities of guanine, thymine and cytosine are accurate; these predictions are currently being probed in our laboratories). Examination of the reactivity of the adenine radical cation toward tetrahydrofuran suggests that this radical cation may be able to abstract a hydrogen atom from a sugar moiety of DNA.

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