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The Influence of Hydrogen Bonding on Hydrogen-Atom Abstraction Reactions of Dehydropyridinium Cations in the Gas Phase

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Abstract

The reactions of several substituted, positively-charged dehydropyridinium cations with cyclohexane, methanol and tetrahydrofuran have been examined in a Fourier-transform ion cyclotron resonance mass spectrometer. All of the charged monoradicals react with the neutral reagents exclusively via hydrogen atom abstraction. For cyclohexane, there is a good correlation between the reaction efficiencies and the calculated electron affinities at the radical sites; that is, the greater the electron affinity of the charged monoradical at the radical site, the faster the reaction. The reaction efficiencies with methanol and tetrahydrofuran, however, do not correlate with the calculated electron affinities. Density functional theory (DFT) calculations indicate that for these reagents a stabilizing hydrogen bonding interaction exists in the hydrogen atom abstraction transition states for some of the charged monoradicals but not for others. At both the MPW1K and G3MP2B3 levels of theory, there is a good correlation between the calculated activation enthalpies and the observed reaction efficiencies although the G3MP2B3 method provides a slightly better correlation than the MPW1K method. The extent of enhancement in the reaction efficiencies caused by the hydrogen bonding interactions parallels the calculated hydrogen bond lengths in the transition states.

Introduction

The mechanisms of hydrogen atom abstraction by radicals have been of interest for decades. 1 The reactivity of aromatic σ -radicals (e.g., phenyl radicals), in particular, has seen renewed interest since the discovery that the biological activity of some powerful anti-tumor antibiotics arises from formation of aromatic σ,σ -biradical intermediates that can abstract hydrogen atoms from sugar moieties in DNA.² However, the parameters that control the reactivity of aromatic σ -radicals are still poorly understood. One of the challenges faced in the examination of the reactivity of these highly reactive intermediates is their short lifetime in solution.^{2c,2g,2h}

Gas-phase studies involve a well-controlled, solvent-free environment that allows the rates of reactions to be controlled by variation of the concentration of the reagent. Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR) has been used to examine the reactivity of various radicals toward neutral reagents.³ These gas-phase studies utilize

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Supporting Information Available: Tables of Cartesian coordinates, electronic energies, zero-point vibrational energies, 298 K thermal contributions, and derived enthalpies for all species. Complete ref. 20. This material is available free of charge via the Internet at <http://pubs.acs.org>.

the “distonic ion” approach that involves studying reactive radicals via their derivatives that carry an inert charged group for manipulation in the mass spectrometer.³

Previous gas-phase studies^{3e,4,5} on aromatic σ -monoradicals and σ,σ -biradicals have suggested that the reactivity of these species depends, at least in part, on the magnitude of the (calculated) electron affinity associated with the radical site(s). Recently, we reported⁶ the results of our gas-phase studies on the isomeric 2-, 3- and 4-dehydropyridinium cations. For these three positively charged, aromatic σ -monoradicals, the relative rates for hydrogen atom abstraction from cyclohexane, methanol, ethanol and tetrahydrofuran (THF) were found to parallel their calculated electron affinities. However, for 2-dehydropyridinium cation, the calculated barrier heights were also found⁶ to be affected by stabilizing hydrogen bonding interactions in the transition states. Here, we report the experimental results for the reactivity of several substituted dehydropyridinium cations (Chart 1) toward cyclohexane, methanol and THF, which were obtained by using an FT-ICR mass spectrometer. Density functional theory (DFT) calculations are used to provide insight into the extent, and nature, of the hydrogen bonding interactions in the transition states of these molecules.

Experimental Methods

All experiments were carried out in a Finnigan FTMS 2001 dual-cell Fourier-transform ion cyclotron resonance mass spectrometer (FT-ICR). This instrument has been described in detail previously.^{3a–d,6} Briefly, the dual cell is aligned collinearly within the magnetic field generated by a 3 T superconducting magnet. The center trapping plate (conductance limit) with a 2 mm hole divides the reaction chamber into two equal, differentially-pumped cells. The vacuum system is operated at a nominal base pressure of $\leq 10^{-9}$ torr in each of the cells, as measured by ionization gauges located on each side of the dual cell. The vacuum is maintained by two Edwards diffusion pumps (800 L s^{-1}), one for each side, backed with Alcatel 2012 mechanical pumps. The instrument is equipped with an Odyssey data acquisition system.

All reagents and the precursors to the ions (2-iodopyridine, 3-iodopyridine, 2-amino-3-nitropyridine, 2-chloro-3-nitropyridine, 2-hydroxy-3-nitropyridine, 3-hydroxy-2-iodopyridine, 4-hydroxy-3-nitropyridine) were commercially available and were used as received. For the generation of charged radicals **b**, **c**, **d**, **e**, **g** and **h** (Chart 1), the corresponding radical precursor was allowed to react for about 3 s with protonated methanol to yield an *N*-protonated iodo- or nitropyridine. For the generation of charged radicals **a** and **f** (Chart 1), 2-iodo-3-hydroxypyridine and 2-iodopyridine, respectively, were allowed to react for 3–10 s with methylated iodomethane to yield the corresponding *N*-methylated iodypyridinium cation. The *N*-protonated (methylated) species were then transferred into the second, clean cell. The transferred molecules were allowed to cool for about one second via collisions with the neutral reagent in the cell (e.g., tetrahydrofuran; ca. 3.9×10^{-8} torr) and via emission of infrared light. The technique of sustained off-resonance irradiated collision-activated dissociation⁷ (SORI-CAD) with argon target gas was used to homolytically cleave the carbon-iodine (C–I) or carbon-nitrogen (C–NO₂) bond. The desired charged radical was isolated by ejecting all other ions via a series of stored-waveform inverse Fourier transform (SWIFT) excitation pulses applied to the plates of the cell.⁸

All reactions studied under the conditions described above follow pseudo-first order kinetics, which allows for the derivation of the second-order reaction rate constant (k_{exp}) from a semilogarithmic plot of the relative abundance of the reactant ion versus reaction time. The theoretical collision rate constants (k_{coll}) were obtained by using a parameterized trajectory theory.⁹ The efficiency of each reaction (the fraction of collisions that leads to reaction) is given by $k_{\text{exp}}/k_{\text{coll}}$.

Computational Methods

Electronic energies and thermally corrected (298 K) enthalpies for all ground-state species and transition states were computed at the G3MP2B3 level of theory.¹⁰ In the G3MP2B3 procedure, molecular geometries are optimized at the density functional (DFT) level of theory by using the 6-31G(d) basis set.¹¹ These DFT calculations use the three-parameter exchange functional of Becke,¹² which is combined with the gradient-corrected correlation functional of Lee, Yang and Parr¹³ (B3LYP). All DFT geometries were verified to be local minima by computation of analytic vibrational frequencies. DFT calculations for doublet states employed an unrestricted formalism and total spin expectation values for Slater determinants formed from the optimized Kohn-Sham orbitals did not exceed 0.77.

In order to compute vertical electron affinities (EA_v) for the charged aryl radicals, the geometries were optimized at the B3LYP level of theory by using the correlation-consistent polarized valence-triple- ζ (cc-pVTZ14) basis set. Note that for the aryl radicals containing a hydroxyl substituent (radicals **a**, **c** and **d**), the geometry optimizations were performed by using the same conformations (i.e., OH group either *syn* or *anti* to the radical site) as those obtained in the transition state calculations (see below). Single-point calculations (B3LYP/aug-cc-pVTZ14) using the optimized geometry for each charged aryl radical were also carried out for the states that are produced when a single electron is added to the nonbonding σ orbital of each molecule.¹⁵ For the charged aryl radicals studied here, these calculations involve (zwitterionic) singlet states.¹⁶ The vertical electron affinities of the charged aryl radicals were computed as $[E_0(\text{monoradical; doublet state})] - [E_0(\text{monoradical} + \text{electron; singlet state})]$. Note that because these are vertical electron affinities, zero-point vibrational energies (ZPVEs) and 298 K thermal contributions to the enthalpy are not included.

Molecular geometries for the charged aryl radicals, cyclohexane, methanol and tetrahydrofuran, as well as the hydrogen-atom abstraction transition states for each of the charged aryl radicals with methanol and tetrahydrofuran, were also optimized at the MPW1K level of theory^{17,18} by using the 6-31+G(d,p) basis set.^{11,19} The MPW1K functional is a modification of the Perdew-Wang gradient-corrected exchange functional, with one parameter optimized to give the best fit to kinetic data for forty radical reactions.¹⁷ All MPW1K geometries were verified to be local minima (or transition states) by computation of analytic vibrational frequencies, and these (unscaled) frequencies were used to compute zero-point vibrational energies (ZPVE) and 298 K thermal contributions ($H_{298} - E_0$) for all species. "Activation enthalpies" for the charged aryl radicals were computed as the difference in enthalpy between the transition state and the separated reactants (i.e., charged aryl radical and either methanol or tetrahydrofuran). MPW1K calculations for the charged aryl radicals and the transition states employed an unrestricted formalism.

All G3MP2B3 and DFT calculations were carried out with the Gaussian 0320 electronic structure program suite.

Results

Gas-phase reactions of the isolated positively charged radicals **a** – **h** were examined with cyclohexane, methanol and tetrahydrofuran. The structures of most of these radicals have been verified in previous studies.^{3c,21} All of the radicals react with the neutral reagents exclusively via hydrogen atom abstraction. G3MP2B3 calculations show that all of the hydrogen atom abstraction reactions between radicals **a** – **h** and the neutral reagents are very exothermic (cyclohexane: $-19.8 - -22.2$ kcal/mol; methanol: $-22.8 - -25.3$ kcal/mol; tetrahydrofuran $-25.6 - -28.1$ kcal/mol). Reaction efficiencies and calculated electron affinities¹⁵ are listed in Table 1. Previous studies^{3e,6} have suggested that abstraction of the

α -hydrogen atom from THF and the methyl hydrogen atom from methanol are thermodynamically favored over the β -hydrogen atom and hydroxyl hydrogen atom, respectively. In all experiments, the decay in the reactant ion population follows pseudo-first order kinetics, which indicates that the ion populations are isomerically pure (typically, about 2% of an unreactive isomer must be present in order to observe deviation from pseudo-first order kinetics). Note that, as a result of a greater number of repeat measurements, the reaction efficiencies for **b** and **g** (Table 1) differ slightly from those reported previously.

Discussion

Reactivity toward cyclohexane

The reaction efficiencies for reactions of the isolated radicals, **a** – **h**, with cyclohexane correlate well with the calculated EAs (Figure 1); that is, the greater the electron affinity of the charged monoradical at the radical site, the faster the reaction. This observation is consistent with previous reports^{4,6} showing that the reactivity of a radical via hydrogen atom abstraction depends, at least in part, on the magnitude of the EA of the radical, and this dependence has been rationalized^{4,6} using polar effects. Polar effects (i.e., stabilization of the transition state by polarization), have been suggested to significantly influence the reactivity of both electrophilic and nucleophilic radicals.^{22,23,24} The ionic avoided curve crossing model developed by Anderson and coworkers,²² in particular, has been used previously^{4,6} to explain the rates of radical reactions such as the ones reported here. Development of this model was inspired by the observation that the transition state energy for hydrogen atom abstraction by radicals, such as OH, Br and Cl, correlates directly with the ionic energy of the separated reactants, which is expressed as the difference in the ionization energy (IE) and the electron affinity (EA) of the reactants (i.e. IE – EA). For a positively charged radical, $R^+Z^\bullet$, (like those studied here) and a neutral reagent, XH, the most important ionic resonance structure of the transition state can be represented as $[R^+Z^-][XH^+]$.^{22,23,24} Increasing the EA of the radical, or decreasing the IE of the neutral reagent, stabilizes this configuration, which results in a lower transition state energy.^{22,23,24} However, note that we have not calculated the transition states for the reactions of radicals **a** – **h** with cyclohexane.

Reactivity toward methanol

Unlike the reactivity of radicals **a** – **h** towards cyclohexane, no correlation was found between the calculated EAs and the measured reaction efficiencies with methanol (Figure 2). However, the calculated activation enthalpies for hydrogen atom abstraction from the methyl group of methanol (Table 2) by radicals **a** – **h** do, in fact, correlate well with the measured reaction efficiencies (Figure 3). Note that for radicals **a** – **h** methyl hydrogen atom abstraction is calculated to be kinetically favored over hydroxyl hydrogen atom abstraction by at least 4.5 kcal/mol (radical **f**) and up to 10.6 kcal/mol (radical **b**) at the MPW1K and G3MP2B3 levels of theory. Examination of the reactions of radical **g** with CD₃OH supports the computational results – only abstraction of a deuterium atom was observed. Such regioselectivity for hydrogen atom abstraction from methanol has also been observed with hydroxyl radical at low temperatures.²⁵ It should also be noted that most of the activation enthalpy values are negative due to the formation of a gas-phase collision-complex stabilized by ion-dipole and ion-induced dipole interactions prior to reaction of the ion with the neutral molecule. Finally, note that the correlation between the calculated activation enthalpies and the measured reaction efficiencies is quite good at both the MPW1K and G3MP2B3 levels of theory (Figure 3).²⁶

The calculated transition state structures (Figure 4) indicate a stabilizing hydrogen bonding interaction with methanol for radicals **a**, **b**, **c**, **d** and **h**, but not for radicals **e**, **f** or **g**. This interaction involves hydrogen bonding between the oxygen atom in methanol and a hydrogen atom in either the NH^+ group (radical **b**) or the amino/hydroxyl substituent group (radicals **a**, **c**, **d** and **h**). Such stabilization is not possible for radicals **e**, **f** or **g**. The significance of stabilizing hydrogen bonding interactions is made especially clear when comparing the reactions of radicals **g** and **h** with methanol. Radical **h**, which benefits from hydrogen bonding with the NH_2 group in the transition state, reacts about five times as fast as radical **g** despite its smaller EA (5.95 and 6.13 eV for radicals **h** and **g**, respectively; Table 1). Finally, it is noteworthy that the length of the hydrogen bond in the transition state appears to reflect the relative degree of stabilization from hydrogen bonding; that is, the shorter the hydrogen bond, the stronger the interaction, the lower the barrier for hydrogen atom abstraction, and consequently, the faster the reaction. For example, radical **d**, which has the shortest hydrogen bond in the transition state (1.6371 Å; Figure 4), has the highest reaction efficiency (48%; Tables 1 and 2) of the radicals studied here.

Reactivity toward tetrahydrofuran

The computational and experimental results for tetrahydrofuran are very similar to those for methanol. For example, no correlation exists between the calculated EAs for radicals **a** – **h** and the measured reaction efficiencies with tetrahydrofuran (Figure 5), but the calculated activation enthalpies for hydrogen atom abstraction from tetrahydrofuran (Table 3; note that the kinetically favored site for hydrogen atom abstraction is from the α -carbon atom of tetrahydrofuran3e) by radicals **a** – **h** do correlate well with the measured reaction efficiencies (Figure 6). Again, this correlation is quite good at both the MPW1K and G3MP2B3 levels of theory (Figure 6).²⁶

Moreover, the calculated transition state structures (Figure 7) indicate a stabilizing hydrogen bonding interaction with tetrahydrofuran for radicals **a**, **b**, **c**, **d** and **h**, but not for radicals **e**, **f** or **g**. Again, the length of the hydrogen bond in the transition state reflects the relative degree of stabilization. For example, radical **d**, which has the shortest hydrogen bond in the transition state (1.5307 Å; Figure 7), has the highest reaction efficiency (88%; Tables 1 and 3) of the radicals studied here.

Conclusions

All of the charged radicals studied react exclusively via hydrogen atom abstraction with cyclohexane, methanol and tetrahydrofuran. The measured reaction efficiencies for the charged radicals with cyclohexane correlate well with the magnitudes of the (calculated) electron affinities, as expected based on previous studies. However, the measured reaction efficiencies for the charged radicals with both methanol and tetrahydrofuran do not correlate with the (calculated) electron affinities but do correlate well with the calculated activation enthalpies (at both the MPW1K and G3MP2B3 levels of theory). For the reactions with the neutral reagents, methanol and tetrahydrofuran, hydrogen bonding interactions between the neutral reagent and either the NH^+ group or the amino/hydroxyl substituent of the charged radical stabilize the transition state, which leads to a higher reaction efficiency than anticipated based only on the magnitude of the electron affinity. The length of the hydrogen bond in the transition state appears to reflect the relative degree of stabilization from hydrogen bonding; that is, the shorter the hydrogen bond, the stronger the interaction, the lower the barrier for hydrogen atom abstraction, and consequently, the faster the reaction. Finally, even though the MPW1K functional has been specifically optimized for radical reactions, G3MP2B3 theory provides slightly better fits between the measured reaction efficiencies and calculated activation enthalpies than MPW1K for the radicals studied here.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. Natural logarithm of the reaction efficiencies for hydrogen-atom abstraction from cyclohexane versus calculated vertical electron affinities (eV) for charged radicals **a – h**. The data are fit to a linear trend line ($R^2 = 0.83$).

Figure 2. Natural logarithm of the reaction efficiencies for hydrogen-atom abstraction from methanol versus calculated vertical electron affinities (eV) for charged radicals **a** – **h**.

Figure 3. Natural logarithm of the reaction efficiencies for hydrogen-atom abstraction from methanol versus calculated activation enthalpies (kcal/mol) for charged radicals **a – h**. MPW1K (circles) and G3MP2B3 (squares) data are fit to linear trend lines ($R^2 = 0.93$ and 0.96 , respectively).

Figure 4.

Calculated (MPW1K) transition-state structures for hydrogen-atom abstraction from methanol by radicals **a** – **h**. Distances between the hydrogen atom being transferred and the α -carbon atom in methanol, distances between the hydrogen atom being transferred and the radical site, and hydrogen bond lengths, are also shown.

Figure 5. Natural logarithm of the reaction efficiencies for hydrogen-atom abstraction from tetrahydrofuran versus calculated vertical electron affinities (eV) for charged radicals **a – h**.

Figure 6. Natural logarithm of the reaction efficiencies for hydrogen-atom abstraction from tetrahydrofuran versus calculated activation enthalpies (kcal/mol) for charged radicals **a – h**. MPW1K (circles) and G3MP2B3 (squares) data are fit to linear trend lines ($R^2 = 0.95$ and 0.97 , respectively).

Figure 7.

Calculated (MPW1K) transition-state structures for hydrogen-atom abstraction from tetrahydrofuran by radicals **a** – **h**. Distances between the hydrogen atom being transferred and the α -carbon atom in tetrahydrofuran, distances between the hydrogen atom being transferred and the radical site, and hydrogen bond lengths, are also shown.

Chart 1.

TABLE 1
 Calculated^a Electron Affinities (EA) and Measured Reaction Efficiencies^b for Hydrogen-Atom Abstraction Reactions of Charged Radicals a – h with
 cyclohexane, Methanol and Tetrahydrofuran

EA, eV	6.85	6.69	6.53	6.48	6.47	6.43	6.13	5.95
34%	35%	34%	27%	28%	21%	19%	17%
CH ₃ OH	18%	22%	40%	48%	5.4%	2.2%	1.7%	9.1%

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a	b	c	d	e	f	g	h	55%
										33%
										34%
										38%
										88%
										72%
										65%
										69%

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culated at the (U)B3LYP/cc-pVTZ//((U)B3LYP/cc-pVTZ level of theory.

tion efficiencies are reported as $k_{\text{reaction}}/k_{\text{collision}} \times 100\%$.

TABLE 2

Calculated Activation Enthalpies^{a,b} (kcal/mol) and Measured Reaction Efficiencies^c for Hydrogen Atom Abstraction by Charged Radicals a – h from Methanol

radical	activation enthalpy, methyl H-atom abstraction	activation enthalpy, hydroxyl H-atom abstraction	reaction efficiency
a	−9.2 (−9.2)	−1.4 (−1.9)	18%
b	−10.6 (−9.8)	−0.3 (0.8)	22%
c	−11.6 (−10.8)	−3.7 (−3.3)	40%
d	−13.2 (−12.2)	−4.7 (−4.3)	48%
e	−4.4 (−4.9)	2.5 (2.2)	5.4%
f	−2.9 (−2.8)	1.6 (2.1)	2.2%
g	−4.5 (−4.0)	1.8 (2.7)	1.7%
h	−7.7 (−7.5)	−1.7 (−1.6)	9.1%

^a“Activation enthalpy” is the difference in enthalpy between the separated reactants and the transition state.

^bCalculated at the MPW1K/6-31+G(d,p) level of theory; values in parentheses calculated at the G3MP2B3 level of theory.

^cReaction efficiencies are reported as $k_{\text{reaction}}/k_{\text{collision}} \times 100\%$.

TABLE 3

Calculated Activation Enthalpies^{a,b} (kcal/mol) and Measured Reaction Efficiencies^c for Hydrogen Atom Abstraction by Charged Radicals a – h from Tetrahydrofuran

radical	activation enthalpy	reaction efficiency
a	−15.2 (−16.6)	69%
b	−17.1 (−17.4)	65%
c	−18.0 (−18.4)	72%
d	−20.4 (−20.5)	88%
e	−8.0 (−10.4)	38%
f	−6.8 (−9.5)	34%
g	−8.6 (−10.1)	33%
h	−12.7 (−13.8)	55%

^a“Activation enthalpy” is the difference in enthalpy between the separated reactants and the transition state.

^bCalculated at the MPW1K/6-31+G(d,p) level of theory; values in parentheses calculated at the G3MP2B3 level of theory.

^cReaction efficiencies are reported as $k_{\text{reaction}}/k_{\text{collision}} \times 100\%$.