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Intramolecular Hydrogen Migration in Ionized Amines: A Theoretical Study of the Gas-Phase Analogues of the Hofmann-Löffler and Related Rearrangements

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Abstract: Ab initio molecular orbital theory using split-valence plus polarization basis sets and incorporating electron correlation has been used to examine the barriers to 1,*n*-hydrogen migration for simple ionized amines, including the radical cations of methylamine, ethylamine, *n*-propylamine, and *n*-butylamine. The barrier heights decrease monotonically on progressing from the 1,2- to the 1,5-hydrogen shift. This smooth trend may be correlated in part with a decrease in ring strain and an increase in linearity of the calculated C---H---N angle in the corresponding transition structures. The calculated barriers and rate constants for hydrogen migration are consistent with facile rearrangements taking place in the gas phase in long-chain amine radical cations.

For some years now we have been studying gas-phase ions with unusual structures, which might formally be derived from their more conventional isomers by a simple hydrogen shift. For example, the methyleneoxonium radical cation $^{\bullet}CH_2OH_2^{+}$ has been shown theoretically[1] and experimentally[2] to be a stable isomer of the methanol radical cation $CH_3OH^{\bullet+}$, and the two species are conceptually related by a 1,2-hydrogen shift:

$$CH_3OH^{\bullet+} \xrightarrow{\text{1,2-H shift}} {}^{\bullet}CH_2OH_2^{+}$$

Similarly, the distonic[3] radical cations $^{\bullet}CH_2CH_2OH_2^{+}$[4a,5] and $^{\bullet}CH_2CH_2CH_2OH_2^{+}$[4b,5] are related to their isomers ethanol$^{\bullet+}$ and propanol$^{\bullet+}$ by 1,3- and 1,4-hydrogen shifts, respectively.

The hydrogen shifts connecting conventional radical cations and their distonic isomers in some cases have important experimental consequences in mass spectrometric studies[6] where they may lead to characteristic fragmentation patterns.[7] For example, it is well-known[7a,8] that aliphatic alcohols will readily lose H_2O in the mass spectrometer. The corresponding rearrangements in the amine radical cations are less important from an analytical point of view[9] since the high-energy ions are more likely to undergo facile α-cleavage reactions (yielding $CH_2NH_2^{+}$) than to lose NH_3. In a review of the literature up to the mid-1970's,[8] only a few reports of NH_3 loss from alkylamines were noted. However, in 1978 Lobanov et al.[10] reported that intramolecular hydrogen migration does occur in the field-ionization mass spectrometry of aliphatic amines. More recently, Hammerum[11] has shown through labeling studies that low-energy amine radical cations produced in a similar manner in the mass spectrometer undergo extensive intramolecular hydrogen shifts prior to fragmentation. These observations have since been confirmed in a number of other gas-phase studies[12-15] which have investigated in more detail the rearrangement reactions of low-energy amine radical cations.

Most of our previous theoretical work on rearrangement reactions in radical cations has been concerned with 1,2-hydrogen shifts, in particular in ylidions.[16] In this paper, we extend our earlier studies to larger systems by examining the rearrangement of primary alkylamine radical cations $CH_3(CH_2)_nNH_2^{\bullet+}$ to their distonic isomers $^{\bullet}CH_2(CH_2)_nNH_3^{+}$ for $n = 0$, 1, 2, and 3. The 1,5-hydrogen rearrangement ($n = 3$) is analogous to the process which occurs in solution in the well-known Hofmann-Löffler reaction.[17,18]

Method and Results

Standard ab initio molecular orbital calculations[19] were carried out with modified versions[20] of the Gaussian 80[21] and Gaussian

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Table I. Calculated Total Energies[a] (hartrees), Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}), Thermal Corrections ($H_{298} - H_0$, kJ mol^{-1}) and Entropies (S_{298}, J mol^{-1} K^{-1}), and Experimental Heats of Formation ($\Delta H_f{}^\circ{}_{298}$, kJ mol^{-1})

species	structure	symmetry	HF/3-21G[b]	HF/6-31G*	MP2/6-31G*	ZPVE[b,c]	$H_{298} - H_0$[b,c]	S_{298}[b,c]	$\Delta H_f{}^\circ{}_{298}$[d]
$CH_3NH_2{}^{\bullet+}$	**1a**	C_s	−94.416 02[e]	−94.932 23[e]	−95.190 44	155.2	13.0	263.0	843
$^{\bullet}CH_2NH_3{}^+$	**1b**	C_s	−94.417 30[e]	−94.930 81[e]	−95.196 74	158.8	12.9	255.9	958[f]
TS(**1a**→**1b**)	**1c**	C_s	−94.322 53[e]	−94.844 01[e]	−95.123 77	145.5	10.9	242.0	
$CH_3CH_2NH_2{}^{\bullet+}$	**2a**	C_s	−133.243 54	−133.975 27	−134.363 65	228.3	16.0	307.6	808
$^{\bullet}CH_2CH_2NH_3{}^+$	**2b**	C_s	−133.253 93	−133.982 89	−134.378 70	233.3	15.5	288.3	770[g]
TS(**2a**→**2b**)	**2c**	C_s	−133.169 81	−133.898 60	−134.308 77	220.5	12.8	269.2	
$CH_3CH_2CH_2NH_2{}^{\bullet+}$	**3a**	C_s	−172.065 76	−173.012 84	−173.532 51	301.3	18.9	322.5	777
$^{\bullet}CH_2CH_2CH_2NH_3{}^+$	**3b**	C_1	−172.079 01	−173.022 83	−173.550 22	306.8	18.1	314.0	745[g]
TS(**3a**→**3b**)	**3c**	C_1	−172.024 52	−172.966 28	−173.506 64	295.7	15.0	292.6	
$CH_3CH_2CH_2CH_2NH_2{}^{\bullet+}$	**4a**	C_s	−210.886 20	−212.047 75[b]	−212.697 97[b]				748
$^{\bullet}CH_2CH_2CH_2CH_2NH_3{}^+$	**4b**	C_1	−210.901 41	−212.058 25[b]	−212.719 72[b]				720[g]
TS(**4a**→**4b**)	**4c**	C_1	−210.863 10	−212.018 28[b]	−212.690 93[b]	369.3	17.7	316.3	

[a] Based on 6-31G* optimized geometries unless otherwise noted. [b] Based on 3-21G optimized geometries. [c] Using calculated vibrational frequencies scaled by 0.9. [d] From ref 36 unless otherwise noted. [e] From ref 39. [f] From ref 37. [g] Estimated value from ref 15.

Table II. Calculated and Experimental Relative Energies (kJ mol^{-1})[a]

species	structure	HF/3-21G	HF/6-31G*	MP2/6-31G*	ΔE_0[b]	ΔH_{298}[c]	ΔG_{298}[d]	exptl[e]
$CH_3NH_2{}^{\bullet+}$	**1a**	0	0	0	0	0	0	0
$^{\bullet}CH_2NH_3{}^+$	**1b**	−3	4	−17	−13	−13	−11	115
TS(**1a**→**1b**)	**1c**	246	232	175	165	163	170	
$CH_3CH_2NH_2{}^{\bullet+}$	**2a**	0	0	0	0	0	0	0
$^{\bullet}CH_2CH_2NH_3{}^+$	**2b**	−27	−20	−40	−35	−35	−29	−38[f]
TS(**2a**→**2b**)	**2c**	194	201	144	136	133	145	
$CH_3CH_2CH_2NH_2{}^{\bullet+}$	**3a**	0	0	0	0	0	0	0
$^{\bullet}CH_2CH_2CH_2NH_3{}^+$	**3b**	−35	−26	−47	−41	−42	−39	−32[f]
TS(**3a**→**3b**)	**3c**	108	122	68	62	58	67	
$CH_3CH_2CH_2CH_2NH_2{}^{\bullet+}$	**4a**	0	0	0				0
$^{\bullet}CH_2CH_2CH_2CH_2NH_3{}^+$	**4b**	−40	−28	−57				−28[f]
TS(**4a**→**4b**)	**4c**	61	77	18				

[a] Based on the total energies in Table I. [b] From eq 1. [c] ΔE_0 plus the difference in $H_{298} - H_0$ values. [d] From $\Delta G_{298} = \Delta H_{298} - T\Delta S_{298}$. [e] Based on the $\Delta H_f{}^\circ{}_{298}$ values in Table I. [f] Includes estimated heat of formation from Table I.

82[22] programs. Optimized structures were obtained with use of gradient procedures[21-23] and the 3-21G basis set.[24] These structures were reoptimized with the 6-31G*[25] basis set, except for the $C_4H_{11}N^{\bullet+}$ system where computational expense precluded the larger calculations. The spin-unrestricted Hartree–Fock (UHF) formalism was used for all systems, and no appreciable spin contamination was encountered. Improved relative energies were obtained with the incorporation of valence-electron correlation using Møller–Plesset theory terminated at second order (MP2).[26] Vibrational frequencies, calculated at the 3-21G//3-21G level and then scaled by 0.9, were used to characterize stationary points on the surface as minima (representing equilibrium structures) or saddle points (representing transition structures) and were also used in the evaluation of thermodynamic properties.

Relative energies at 0 K for equilibrium structures and transition structures were obtained from the equation

$$\Delta E_0 = \Delta E(\mathrm{MP2/6\text{-}31G^*}) + \Delta(\mathrm{ZPVE}) \qquad (1)$$

where ZPVE refers to the zero-point vibrational energy. Unless stated otherwise, these are the values given in the text. Temperature corrections to the relative enthalpies ($H_{298} - H_0$) and absolute entropies (S_{298}) were calculated with standard formulae,[19,27] leading to values of ΔH_{298} and ΔG_{298}.

Classical transition-state theory (TST)[28] was used to obtain approximate rate constants (k) for the hydrogen shifts from the relation

$$k = (k_BT/h)(Q^{\ddagger}/Q)\exp(-\Delta E^{\ddagger}{}_0/RT) \qquad (2)$$

where the symbols have their usual meaning[29] and, in particular, $\Delta E^{\ddagger}{}_0$ is the barrier height calculated via (1). Within this framework, the activation energy that would be measured experimentally for a unimolecular reaction is given approximately by

$$E_a = \Delta H^{\ddagger}{}_T + RT \qquad (3)$$

Since tunneling may be important for these hydrogen-shift reactions, we have also calculated a simple tunneling correction due to Wigner;[30]

$$\kappa = 1 + u^2/24 \qquad (4)$$

where $u = h\nu_i{}^{\ddagger}/k_BT$ and $\nu_i{}^{\ddagger}$ is the imaginary frequency at the saddle point. With the inclusion of the tunneling correction, eq 2 and 3 become

$$k^* = \kappa k \qquad (5)$$

and

$$E_a{}^* = E_a - RT\ln\kappa \qquad (6)$$

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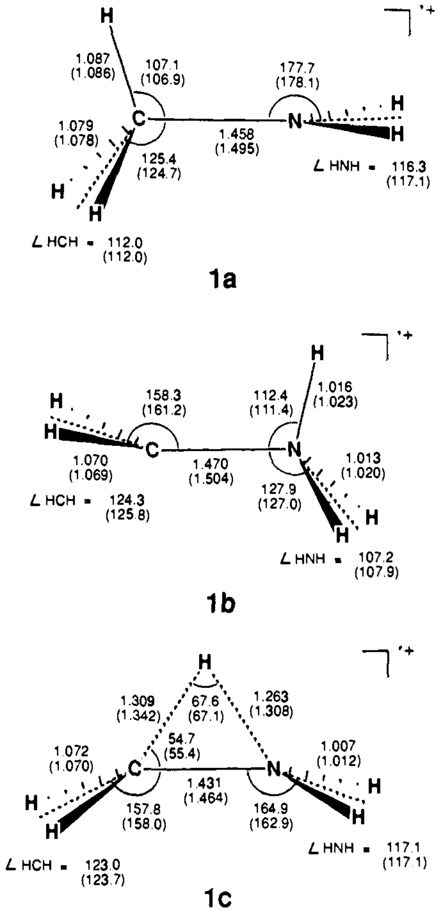

Figure 1. Optimized structures for the $CH_5N^{•+}$ (**1**) system.

Table III. Barriers and Rates for Hydrogen Shifts in Ionized Alkylamines

rearrangement		$\nu_i^{*\,a}$	κ^b	barriers $E_a^{*\,c}$	barriers E_a(exptl)^d	rates $k^{*\,e}$
1,2-shift	**1**	2168	5.56	162		5.7×10^{-17}
1,3-shift	**2**	2017	4.95	132	≥76	7.2×10^{-12}
1,4-shift	**3**	1846	4.31	57	<38	4.2×10^{1}
1,5-shift	**4**	1490	3.15	9^f	<12	

^{a}Calculated imaginary frequency (cm^{-1}) for the transition structure (scaled by 0.9). ^{b}Tunneling correction from eq 4. ^{c}Activation energy (kJ mol^{-1}) calculated at 298 K from eq 6. ^{d}Experimental estimate (kJ mol^{-1}) from ref 15. ^{e}Rate constant (s^{-1}) calculated at 298 K from eq 5. ^{f}Calculated using an estimated ΔH_{298}^* value of 9 kJ mol^{-1}.

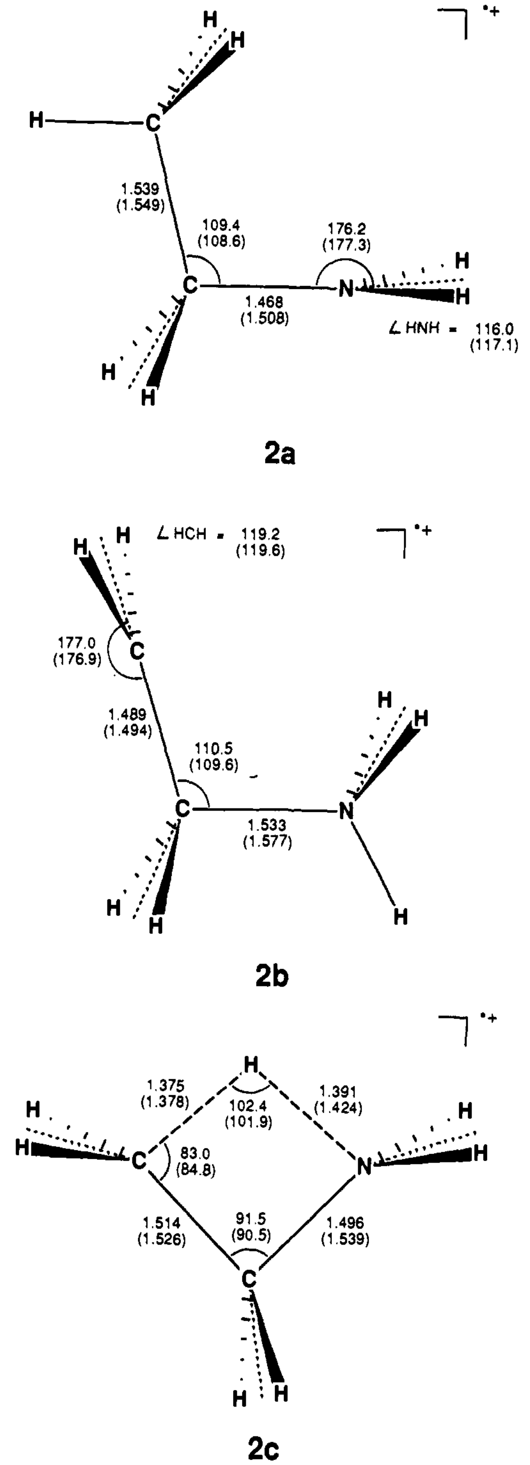

Figure 2. Optimized structures for the $C_2H_7N^{•+}$ (**2**) system.

Although more sophisticated methods are available for treating the reaction rates of unimolecular processes,[31-34] the crude picture presented here is probably adequate for allowing relative comparisons to be made.

Calculated total and relative energies are presented in Tables I and II, respectively, for the alkylamine radical cations (**1a–4a**), their distonic isomers (**1b–4b**), and the transition structures (**1c–4c**) for the hydrogen shifts which connect them. The corresponding optimized structures (6-31G* with 3-21G values in parentheses) are displayed as Figures 1–4 within the course of the discussion. Bond lengths are given in angstroms and angles in degrees. Although full geometry optimizations were carried out for all species, for the sake of clarity only the skeletal parameters are shown in Figures 2–4.[35] Schematic energy profiles for the hydrogen shifts (based on MP2/6-31G* relative energies) are shown in Figure 5. Rate constants and activation energies are presented in Table III.

Experimental heats of formation for the conventional isomers[36] and for the methyleneammonium radical cation (**1b**)[37] are included in Table I. Values for the heats of formation of **2b–4b** were taken

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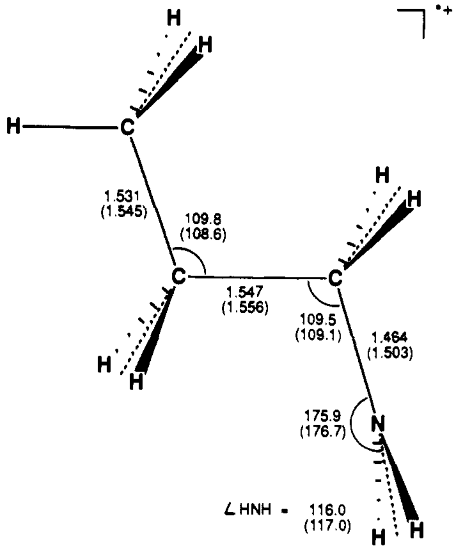
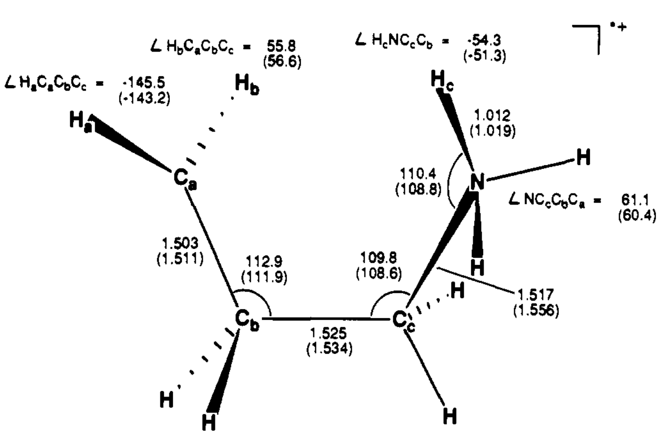
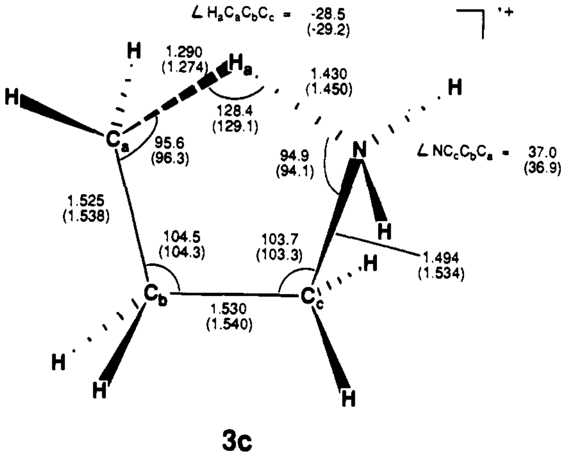


3a



3b



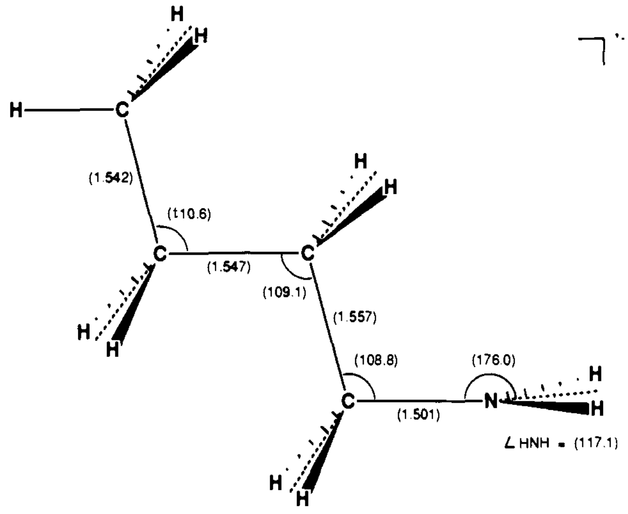
3c

Figure 3. Optimized structures for the $C_3H_9N^{\bullet+}$ (3) system.

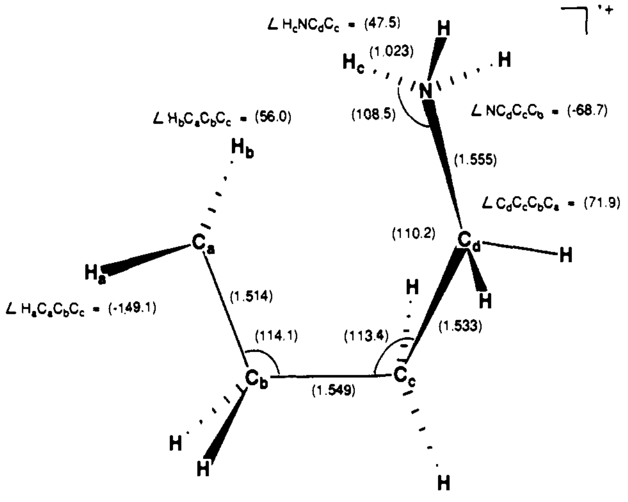
from the work of McLafferty and co-workers,[15] who obtained estimates using an approximate thermochemical scheme. Relative energies based on these values are compared with our ab initio results in Table II.

Discussion

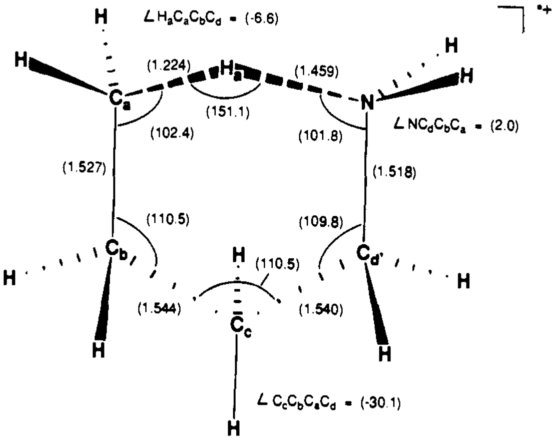
$CH_5N^{\bullet+}$. The optimized structures for the methylamine (**1a**) and methyleneammonium (**1b**) radical cations and for the transition structure connecting them (**1c**) are shown in Figure 1.[38] At the level of theory used here, there is quite a large discrepancy between the theoretical and experimental values for the relative energy of **1a** and **1b** (Table II), and this discrepancy remains even with very high level ab initio calculations,[39,40] the latter yielding



4a



4b



4c

Figure 4. Optimized structures for the $C_4H_{11}N^{\bullet+}$ (4) system.

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[38] A comprehensive bibliography of previous studies on this system is contained in ref 16c.

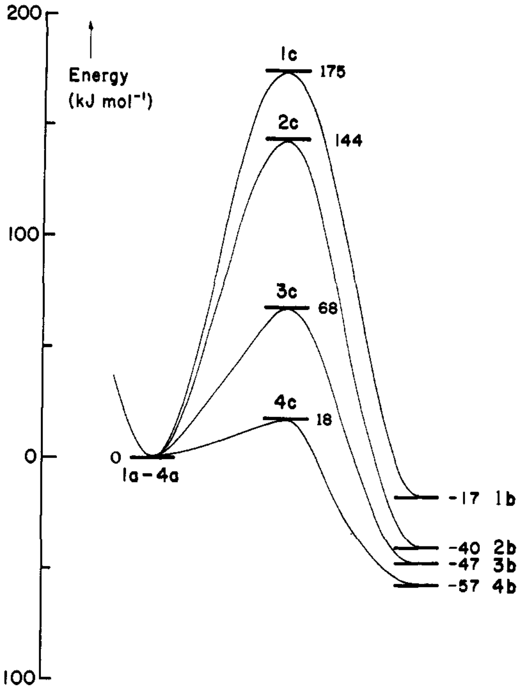

Figure 5. Schematic energy profiles for the hydrogen shifts in the alkylamine radical cations (**1**, 1,2-shift; **2**, 1,3-shift; **3**, 1,4-shift; **4**, 1,5-shift).

-8 kJ mol^{-1} for the energy difference. The barrier height ($\Delta E^{\ddagger}_0$) for the 1,2-hydrogen shift is calculated to be 165 kJ mol^{-1}. Our previously published higher level calculations[39] show that the effects on the barrier height of using the larger 6-31G** basis set (-10 kJ mol^{-1}) and the more complete MP3 treatment of electron correlation ($+13$ kJ mol^{-1}) tend approximately to cancel, giving a best value of 168 kJ mol^{-1} for $\Delta E^{\ddagger}_0$.

$C_2H_7N^{\cdot+}$. The optimized structures for the $C_2H_7N^{\cdot+}$ system are shown in Figure 2. We have previously reported some preliminary calculations for the ethylamine (**2a**) and ethyleneammonium (**2b**) radical cations.[3b,16a] Experimentally, the distonic radical cation **2b** has been observed by a number of workers[12a,15,37,41,42] and confirmed to be a stable isomer of **2a**. Our calculated energy difference (ΔH_{298}) between **2a** and **2b** of -35 kJ mol^{-1} (Table II) is close to the value (-38 kJ mol^{-1}) estimated in ref 15. $\Delta E^{\ddagger}_0$ for the 1,3-hydrogen shift is calculated to be 136 kJ mol^{-1}. Higher level calculations[43] give a barrier at the MP3/6-31G** level of 137 kJ mol^{-1}.

$C_3H_9N^{\cdot+}$. The optimized structures for the $C_3H_9N^{\cdot+}$ system are shown in Figure 3. We have reported some preliminary calculations for the propylamine (**3a**) and trimethyleneammonium (**3b**) radical cations previously,[3b,16a] while more recently evidence for the existence of the distonic radical cation **3b** has come from several mass spectrometric experiments.[15,42,44] We calculate that **3b** lies 42 kJ mol^{-1} below **3a** (ΔH_{298}, Table II), which is again close to the estimate (32 kJ mol^{-1}) from ref 15. It should be noted that we report here only the results for the lowest energy conformations that we have found for the two isomers. For the level of theory used here, these correspond to an all-trans arrangement of the heavy atoms for **3a** and a gauche arrangement for **3b**. The alternative gauche and all-trans conformations lie 3 and 9 kJ mol^{-1} higher in energy than **3a** and **3b**, respectively. $\Delta E^{\ddagger}_0$ for the 1,4-hydrogen shift connecting **3a** with **3b** is calculated to be 62 kJ mol^{-1}.[45] We would expect that this value is unlikely to change significantly with higher level calculations, based on our observations for the $CH_5N^{\cdot+}$ and $C_2H_7N^{\cdot+}$ systems.

$C_4H_{11}N^{\cdot+}$. We have reported previously[3b,16a] some preliminary results for the butylamine (**4a**) and tetramethyleneammonium (**4b**) radical cations. Observation and structural characterization of **4b** in the mass spectrometer was recently reported by McLafferty and co-workers.[15] Our present optimized structures are displayed in Figure 4. Computational expense has prevented us from optimizing the structures of all of the possible conformations for **4a** and **4b**. Of the structures for **4a** with NCCC gauche, we examined in detail the conformation in which, in addition, CCCC is gauche. This was found to lie 4 kJ mol^{-1} (at MP2/6-31G*//3-21G) higher in energy than the all-trans arrangement shown in Figure 4. For the distonic isomer (**4b**), three different gauche conformations were optimized in addition to the all-trans structure. The lowest energy conformation found for **4b** is the gauche arrangement shown in Figure 4, which lies 16 kJ mol^{-1} (at MP2/6-31G*//3-21G) lower in energy than the all-trans structure.

The barrier for the 1,5-hydrogen shift connecting **4a** with **4b** is calculated to be 18 kJ mol^{-1} at MP2/6-31G*. Although we were able to obtain vibrational frequencies for the transition structure **4c**, it did not seem warranted to complete these computationally expensive calculations for the stable isomers **4a** and **4b**, largely for the purpose of obtaining small temperature and vibrational energy corrections to the calculated relative energies. Nevertheless, by examining the results for the other systems in Table II, we may estimate that the inclusion of zero-point vibrational contributions would lower the rearrangement barrier by about 4 kJ mol^{-1}.[46] $\Delta E^{\ddagger}_0$ for the 1,5-hydrogen shift should therefore be $\sim$14 kJ mol^{-1}. Similarly, we would estimate that the energy difference ΔE_0 between **4a** and **4b** is $\sim$50 kJ mol^{-1} in favor of **4b**.

We note that the 1,4-hydrogen shift from **4a** (yielding the distonic $CH_3CH^{\cdot}CH_2CH_2NH_3^{+}$) might in principle be expected to compete with the 1,5-process.[15] However, on the basis of our results for the 1,4-hydrogen shift in the propylamine radical cation (**3a**), we would expect that it will require greater energy than the 1,5-shift.

Barriers and Rates for Hydrogen Migration. We note initially that there is very little difference between the calculated barrier heights for hydrogen migration at 0 K (where $\Delta E^{\ddagger} = \Delta H^{\ddagger} = \Delta G^{\ddagger}$) and the temperature corrected estimates $\Delta H^{\ddagger}_{298}$ and E_a (Tables II and III).[47]

Figure 5 clearly shows that the barriers for the hydrogen shifts in the alkylamine radical cations decrease in the order 1,2- > 1,3- > 1,4- > 1,5-shift with the activation energy for the 1,5-shift (the analogue of the Hofmann–Löffler reaction) being only $\sim$9 kJ mol^{-1} (Table III). This is consistent with the experimental observations[11,12a,13a,14] that hydrogen shifts in ionized alkylamines are generally observed only when the heavy-atom chain length is greater than four. Recently, the activation energies for the 1,3-, 1,4-, and 1,5-hydrogen shifts have been estimated experimentally by McLafferty and co-workers[15] and their results are compared with our theoretical values in Table III. There is rough agreement between the two sets of results, although the theoretical values tend to be somewhat greater than those from experiment. This may be due in part to the (small) amount of excess internal energy that would be possessed by the metastable ionized species.

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(46) Zero-point vibrational contributions lower the energies of the hydrogen shift barriers by 10, 8 and 6 kJ mol^{-1} in the $CH_5N^{\cdot+}$, $C_2H_7N^{\cdot+}$, and $C_3H_9N^{\cdot+}$ systems, respectively.

(47) Strictly speaking, the transition structure for the hydrogen shift process at 298 K should really correspond to the saddle point on the ΔH or ΔG surface at this temperature. For a recent discussion of the temperature dependence of the transition structure, see: Doubleday, C.; McIver, J.; Page, M.; Zielinski, T. *J. Am. Chem. Soc.* **1985**, *107*, 5800.

A number of observations may be made concerning the ease of hydrogen transfer in the systems studied here. First, significant ring strain would be expected in the 3- and 4-membered-ring transition structures involved in the 1,2- and 1,3-shifts. The effect of this ring strain would account to a large extent for the change in our $\Delta H^{\ddagger}_{298}$ values (Table III) which show a dramatic decrease as the ring size of the transition structure increases. Although the decrease in ring strain favors the 1,5-shift over the 1,4-shift, this effect becomes less important for larger cyclic transition structures.[48]

Second, early studies on the Hofmann–Löffler reaction suggested that the hydrogen-shift barrier height might be correlated in part with the closeness to linearity of the C---H---N angle (θ) reached during the transfer process.[17a,49] In the present work, θ is calculated to be 68°, 102°, 128°, and 151° for the 1,2-, 1,3-, 1,4-, and 1,5-shifts, respectively. Although θ does indeed tend toward 180°, this may to some extent simply be a byproduct of the increase in ring size of the transition structure. On the other hand, calculations on the model process

$$\mathrm{CH_4 + NH_3^{\cdot+} \rightarrow [CH_3\text{---}H\text{---}NH_3^{\cdot+}]^{\ddagger} \rightarrow CH_3^{\cdot} + NH_4^{+}}$$

do show[50] that linear hydrogen transfer is favored, and the fact that $\theta < 180°$ for the alkylamine radical cations might be rationalized[17a] in terms of a desire to minimize strain on the other angles in the transition structure. We note that our calculated transfer angle for the prototype Hofmann–Löffler reaction (the 1,5-shift) is 151°. In a recent molecular mechanics study of the related Barton reaction, it was suggested[18c] that the corresponding C---H---O angle is closer to 180°.

Third, as the ring size of the transition structure increases, entropy loss due to cyclic interaction should become increasingly unfavorable.[51] This loss of entropy is expected to be least important in the formation of the three-membered-ring transition structure and to be only modest for the other small rings.[48b,51] This is borne out by our calculated $\Delta S^{\ddagger}_{298}$ values, which are −21, −38, and −30 kJ mol^{-1} for the 1,2-, 1,3-, and 1,4-shifts, respectively. For longer range shifts, the entropy factor is expected to become more significant.

While a consideration of these three factors suggests that 1,5-shifts will dominate hydrogen migrations in alkylamine radical cations,[52] evidence has nevertheless been presented for the more distant 1,6-, 1,7-, and 1,8-shifts, both in solution[17a,d] and in the gas phase.[12d] We note in passing that it does not appear as though orbital symmetry considerations play a major role in the rearrangements of alkylamine radical cations.[53]

Not surprisingly, the calculated rate constants for the hydrogen migrations increase dramatically in the order 1,2- < 1,3- < 1,4-shift (Table III), with the value for the 1,4-shift being ~40 s^{-1}. The tunneling effects (as measured by κ, Table III) are quite substantial, and the simple Wigner correction may be inappropriate for these reactions. Although no corresponding experimental rate constants for the ionized alkylamines are available, values for the gas-phase 1,4- and 1,5-hydrogen shifts in hexanol radical cation have been roughly estimated (for low energy $M^{\cdot+}$) to be $<10^3$ and $\sim 10^5$ s^{-1}, respectively.[54] These results are consistent with the accepted view that gas-phase hydrogen shifts are more facile in ionized alcohols than in amines.[9,55]

Conclusions

We have shown that barrier heights for hydrogen shifts in unbranched primary alkylamine radical cations decrease in the order 1,2- > 1,3- > 1,4- > 1,5-hydrogen shift. The increasing ease of hydrogen migration in these systems parallels the decreasing ring strain and increasing linearity of the C---H---N angle in the corresponding transition structures. For the gas-phase prototype of the Hofmann–Löffler reaction (the 1,5-shift), hydrogen transfer occurs at a predicted angle of 151°. Finally, the calculated barriers and rate constants for the hydrogen rearrangements are consistent with experimental evidence for the occurrence of facile 1,5-hydrogen shifts in ionized amines and for the absence, generally, of 1,2-, 1,3-, and 1,4-shifts.

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