this work, the stable associative complex is the closest we approach the equilibrium condition. Thus, if we interpret the difference in heats of formation between the transition state and the associative complex to be the activation energy for the reaction as it would proceed in the melt, any error that we obtain would be due primarily to our incomplete modelling of the melt structure. A better, more complete modelling of the melt structure, involving introduction of more ions around the reacting species into the calculation, should yield a more accurate answer. We do note that our best modelling of the melt in this work, the stack model, produced a predicted activation energy of 13 kcal mol^{-1}, very close to the apparent experimental value. It is also significant that each step we took to more realistically model the environment of the reactants decreased the difference between the experimental and calculated energy activation.

Conclusions

The Al$_2$Cl$_7^-$ anion is predicted to be a bent, effectively C_{2v} structure. This prediction is invariant to a variety of ionic environments around the anion. In addition, the barrier to inversion at the bridging chlorine is too high to conclude that a linear-averaged structure could have been observed in vibrational spectra of this anion. Our calculated vibrational frequencies and transition dipole moments for the anion agree well with available experimental data. Previous interpretations of the observed vibrational spectra indicating D_{3d} symmetry can be understood in light of the fact that many of the vibrational frequencies are too close together and broadened by interactions with the alkali couterions to be readily observed as separate bands. The excellent agreement between the observed IR spectrum and the MNDO calculated spectrum (including the predicted intensities) confirms that the MNDO method can be very useful in interpretation of IR spectra of similar systems.

The use of sparkles in MNDO seems to be an effective way of modelling ionic interactions in molten salts. They are effective in shielding reacting species of the same charge from each other until they get close enough to react, as one would expect in the true melt. Modelling the structure of the melt with a combination of the sparkles for positive charges and additional AlCl$_4^-$ anions appears to be a promising way to study melt structure and reactions which take place in the melt.

On the basis of our admittedly incomplete model of the melt, the exchange reaction between AlCl$_4^-$ and Al$_2$Cl$_7^-$ is probably the reaction which causes the ^{27}Al NMR line shape behavior in the MEICl/AlCl$_3$ system. The predicted activation energy for this reaction is very close to the experimental value.

We are continuing calculations on improved models of the melt. We are adding a larger number of ions in the ionic environment of the reacting species. In addition, we will also attempt to actually use the imidazolium cation itself in the calculation as the counterion. Either or both of these improvements should allow us to obtain even better estimates of melt structures and the energetics of reactions taking place in the melts.

An ab Initio Molecular Orbital Study on Rearrangement/Fragmentation Processes of Isomeric CH$_3$N$^+$· Ions

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Abstract: The potential energy surface of the CH$_3$N$^+$· system has been investigated using ab initio molecular orbital theory. In accordance with experiment it is found that the two isomers, methylenimine radical cation, CH$_2$NH$^+$· (**1**), and aminomethylene cation, CHNH$_2^+$· (**2**), are found to be separated by a high-energy barrier (239 kJ mol^{-1}) which largely prevents them from isomerizing prior to microsecond fragmentation. However, contrary to previous interpretations, it is argued that the isomer CNH$_2^+$ is not formed in the course of H· loss from CH$_3$N$^+$· under mass spectrometric conditions.

Introduction

During the last few years, the structure/reactivity problem of gaseous radical cations has received renewed attention. It has been demonstrated that in addition to the molecular ion, other ionic isomers exist for which the neutral counterparts are unknown. These structurally intriguing isomers are often found to have comparable if not lower heats of formation. Particular cases concern the so-called *distonic* ions,[1a] species which contain both hyper- and hypovalent structure, and which do not obey the classical valence rules.[1]

A case in point concerns CH$_3$N$^+$· isomers, which have been thoroughly investigated experimentally by Burgers et al.[2] By means of collisional activation (CA) mass spectrometry, isotopic labeling, and thermochemical measurements, Burgers et al.

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(1) (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) For a recent review and leading references, see: Schwarz, H. *Mass Spectrosc. (Tokyo)* **1984**, *32*, 3.
(2) Burgers, P. C.; Holmes, J. L.; Terlouw, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 2762.

demonstrated that in addition to the conventional isomer, i.e., ionized formaldimine, $CH_2NH^{+\cdot}$ (**1**), there exists a second low-energy isomer of unconventional structure, i.e., aminomethylene cation, $CHNH_2^{+\cdot}$ (**2**). Furthermore, **1** and **2** show quite different unimolecular dissociation characteristics in the microsecond time frame, which indicates that there is a relatively high energy barrier preventing **1** and **2** from facile interconversion.

In order to learn more about this small, but fundamentally important chemical system, we have investigated the CH_3N^+ potential energy surface by using quantum chemical methods. By calculating the most relevant part of it, we seek to find a unique theoretical model to rationalize all the existing experimental results. A strong motivation for this work is that some of the species involved seem to play an important role in the interstellar production of organic molecules.[3]
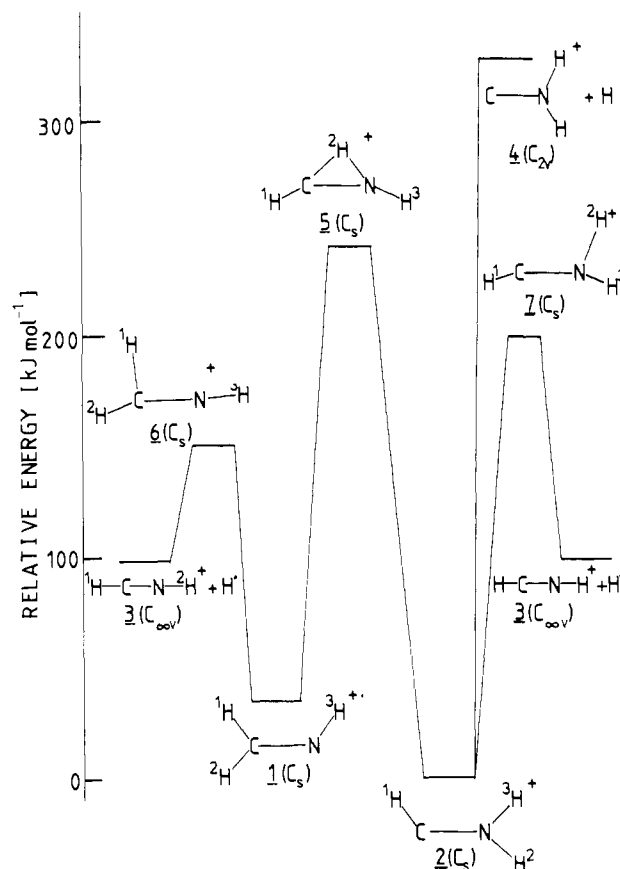
Computational Methods

The calculations were performed by using the standard spin-unrestricted Hartree–Fock formalism. Geometry optimizations were done using the 4-31G atomic bais set.[4] A modified version of the GAUSSIAN 76 series of programs[5] was used throughout, except for the optimizations of the transition-state geometries, for which the GRADSCF program[6] was employed. The force constant matrices were calculated for all stationary points of the potential energy hypersurface and were checked for the correct numbers of negative eigenvalues. The vibrational frequencies obtained were scaled by a factor of 0.9 before calculating the zero-point vibrational energy (ZPVE) in order to account for the fact that the normal frequencies are overestimated at the HF level by 10%.[7] Based on the 4-31G geometries, single point calculations were performed using the larger 6-31G* basis set.[8] In order to further improve the reliability of the calculations, Møeller–Plesset perturbation theory to second order was performed.[9] The level of approximation used to obtain our "best results" may in standard notation be referred to as (MP2/6-31G*//4-31G). The results are presented in Table I and Figure 1. Geometries of optimized structures are given in Figure I.

Results and Discussion

In agreement with the recent calculations of Frisch et al.[10] on $CH_3N^{+\cdot}$ species, the isomer $CH_2NH^{+\cdot}$ (**1**) is calculated to be higher in energy than $CHNH_2^{+\cdot}$ (**2**) by 37 kJ mol⁻¹. However, there exists a discrepancy with the experimentally obtained values according to which **1** is more stable than **2** by 25 kJ mol⁻¹. We do not believe that all of this difference can be accounted for by deficiencies in the quantum chemical approximation used here. The heat of formation data given by Burgers et al.[2] are obtained indirectly through appearance energy measurements of *second* generation ions and may therefore contain significant contributions from kinetic shifts.[11]

To establish the validity of our calculations on the possible fragmentation products $CHNH^+$ (**3**) and CNH_2^+ (**4**), we have compared our data with those obtained by Conrad and Schaefer[12] who used a completely different quantum chemical approach, based on configuration interaction (single and double excitations) using a double-ζ basis set which included polarization functions. They report **4** to lie 193 kJ mol⁻¹ higher than **3**, compared with

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(10) Frisch, M. J.; Raghavachari, K.; Pople, J. A.; Bouma, W. J.; Radom, L. *Chem. Phys.* **1983**, *75*, 323.

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(12) Conrad, M. P.; Schaefer, H. F., III *Nature (London)* **1978**, *274*, 456.

Figure 1. Ground-state potential energy surface for isomerization/dissociation reactions of $CH_3N^{+\cdot}$ isomers as calculated by MP2/6-31G**//4-31G + ZPVE. Geometrical data are as follows (bond lengths in angströms, bond angles in degrees). **1**: C–H(1), 1.080; C–H(2), 1.077; C–N, 1.251; N–H(3), 1.006; H(1)–C–N, 120.2; H(2)–C–N, 119.6; C–N–H(3), 152.3. **2**: C–H(1), 1.071; C–N, 1.258; N–H(3), 1.009; N–H(2), 1.008; H(1)–C–N, 133.2; H(3)–N–C, 123.1; C–N–H(2), 121.5. **3**: C–H(1), 1.067; C–N, 1.124; N–H(2), 0.997. **4**: C–N, 1.241; N–H, 1.020; C–N–H, 122.5. **5**: C–H(1), 1.073; N–H(3), 1.008; C–N, 1.225; C–H(2), 1.345; N–H(2), 1.306; H(1)–C–N, 141.8; C–N–H(3), 147.4. **6**: C–H(1), 1.823; C–H(2), 1.069; C–N, 1.150; N–H(3), 0.998; H-(1)–C–N, 108.6; H(2)–C–N, 159.4; C–N–H(3), 174.5. **7**: C–H(1), 1.068; C–N, 1.165; N–H(2), 1.720; N–H(3), 1.003; H(1)–C–N, 171.0; C–N–H(3), 148.9; C–N–H(2), 119.9.

our energy difference of 228 kJ mol⁻¹. From Table I it can further be seen that the endothermicity of the reaction $HCNH_2^{+\cdot}$ (**2**) → $HCNH^+$ (**3**) + H· is well reproduced in our calculations (98 vs. 84 kJ mol⁻¹).

Our results show that the transition-state (TS) energies for the energetically most feasible unimolecular fragmentation of either **1** and **2**, i.e., TS_6 and TS_7, are lower in energy than the one for their mutual isomerization via TS_5 (see also Figure 1). This finding lends strong support to the assumption that the observed differences in the unimolecular behavior of $CH_3N^{+\cdot}$ ions produced from different neutral precursors are indeed due to two different isomers generated. There is also reasonable quantitative agreement between the experimentally and computatinally determined activation energies for the reaction **2** → **3** (227 vs. 196 kJ mol⁻¹). No experimental value, however, exists for the barrier **1** → **3**, but one should expect it to be significantly smaller than the barrier **2** → **3**. Firstly, Burgers et al.[2] have measured a much lower kinetic energy release for this reaction, and secondly, a lower activation energy for addition of a hydrogen atom to the more electropositive center should be expected.[13]

(13) Burgers, P. C.; Holmes, J. L.; Terlouw, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 642. (b) For a different interpretation of the origin of different activation energies for hydrogen atom addition at the carbon vs. heteroatom centers of ions, see: Frenking, G.; Heinrich, N.; Koch, W.; Schwarz, H. *Chem. Phys. Lett.* **1984**, *105*, 490.

Table I. Total Energies (hartrees), Relative Energies, E_{rel}, and Zero-Point Vibrational Energies, ZPVE (both in kJ mol^{-1}), for $CH_3N^{+\cdot}$ Isomers and Transition States (TS) for Isomerization and Dissociation Pathways[a]

structure	4-31G	6-31G*	MP2/6-31G*	ZPVE	E_{rel}			
					4-31G	6-31G*	MP2/6-31G*	exptl[b]
$CH_2NH^{+\cdot}$ (1)	-93.583 69	-93.717 17	-93.898 25	93.4	17	13	37	-25
$CHNH_2^{+\cdot}$ (2)	-93.593 12	-93.725 20	-93.915 39	101.6	0	0	0	0
$CHNH^+$ (3) + H·	-93.520 58[c]	-93.657 02[c]	-93.866 98[c]	72.9	161	150	98	84
CNH_2^+ (4) + H·	-93.454 66[c]	-93.591 86[c]	-93.778 08	67.7	329	316	326	247
TS (5) 1 → 2	-93.460 90	-96.605 50	-93.815 76	80.0	325	292	239	>247[d]
TS (6) 1 → 3	-93.506 89	-93.641 70	-93.845 57	71.4	196	189	153	
TS (7) 2 → 3	-93.496 40	-93.630 22	-93.829 09	72.0	224	219	196	227

[a] Geometries were optimized using the 4-31G basis set. [b] In kJ mol^{-1}, taken from ref 2. [c] The energy of H· alone is $E = -0.498\,23$ hartrees. [d] This value has been inferred indirectly (ref 2).

The next two factors to be considered are (i) the height of the barrier of interconversion of $CH_2NH^{+\cdot}$ (1) and $CHNH_2^{+\cdot}$ (2), and (ii) the proposed[2] metastable ion reaction 2 → 4. From Figure 1 it is obvious that the reaction to give $CNH_2^{+\cdot}$ (4) is without reverse activation energy and is 80 kJ mol^{-1} *more* endothermic than the value given by Burgers et al.[2] Even if one takes into account the high uncertainty given for the experimental number, we judge the difference to be significant. According to our model, $CNH_2^{+\cdot}$ ions should not be produced from metastable $CHNH_2^{+\cdot}$ ions; in contrast, the latter should either fragment directly to give $CHNH^+$ (3) or undergo a rate-determining isomerization to 1 followed by a fast fragmentation to 3.[14] Because of the relatively small energy difference between the transition states for these two processes (<45 kJ mol^{-1}), it is likely that both are involved in the chemistry of metastable $CHNH_2^+$ (2) ions. Indeed, the reported[2] appearance energies for D· loss (14.0 ± 0.4 eV) and H· loss (13.8 ± 0.1 eV) from $CDNH_2^{+\cdot}$ support this interpretation. Furthermore, both metastable peaks for H· loss from $CDNH_2^{+\cdot}$ and $CHNH_2^{+\cdot}$ shown in ref 2 seem to be composite,[15] although the contribution from the narrow peak is smaller for the former. This last observation is in accordance with the occurrence of the isomerization $CDNH_2^{+\cdot} \rightarrow CDHNH^+$ followed by elimination of *either* D· or H·.

The last part of our discussion is concerned with the question of generating CNH_2^+ (4) from $CH_3N^{+\cdot}$ species. CNH_2^+ (4) has been proposed to play a key role in the interstellar formation of hydrogen isocyanide, HNC.[12,16] Although from the discussion of the previous paragraph we conclude that CNH_2^+ is unlikely to be produced in metastably dissociating $CH_3N^{+\cdot}$ ions, the CNH_2^+ species 4 may well be produced at shorter lifetimes (ion source fragmentations) or under other experimental conditions generating energy-rich precursors. It is important to notice that although the combined system CNH_2^+ (4) + H· is predicted not to have a barrier for the reverse exothermic reaction to give $CHNH_2^+$, this does not preclude the existence of CNH_2^+, which is predicted by the calculations to exist in a potential minimum. As long as the concentration of H· is too low to allow bimolecular reactions, CNH_2^+ may survive for a long time on its own, once it has been formed.[17] However, we do not agree that the evidence presented in ref 2 (partial CA mass spectra) positively identifies the long-sought CNH_2^+ species. The only species which was yet unambiguously identified[2,18] corresponds to $HCNH^+$ (3).[19]

Registry No. 1, 2053-29-4; **2**, 89302-94-3.

(14) For a most recent example for the existence of two-step processes of this kind and leading references, see: (a) Bouma, W. J.; Nobes, R. H.; Radom, L. *Org. Mass Spectrom.* **1982**, *17*, 315. (b) Eckart. K.; Zummack, W.; Schwarz, H. *Ibid.* **1984**, *19*, 642.

(15) In fact, it is hard to decide whether the peak for H· loss from $DCNH_2^{+\cdot}$ reproduced in Figure 2c of ref 2 is truly composite. If this is not the case, the preferred loss of H· could be accounted for (as suggested by a referee) by assuming that the transient, highly excited methylenimine radical cation behaves nonergodically, favoring the elimination of the migrated atom. For convincing examples of nonergodic behavior of polyatomic ions in the gas phase, see: (a) Depke, G.; Lifshitz, C.; Schwarz, H.; Tzidony, E. *Angew. Chem., Int. Ed. Engl.* **1981**, 20, 792. (b) Lifshitz, C. *J. Phys. Chem.* **1983**, *87*, 2304. (c) Tureček, F.; McLafferty, F. W. *J. Am. Chem. Soc.* **1984**, *106*, 2525.

(16) (a) Herbst, E.; Klemperer, W. *Astrophys. J.* **1973**, *185*, 505. (b) Watson, W. D. *Astrophys. J. Lett.* **1973**, *183*, L 17. (c) Pearson, P. K.; Schaefer, H. F., III *Astrophys. J.* **1974**, *192*, 33. (d) Brown, R. D. *Nature (London)* **1977**, *270*, 39.

(17) Unimolecular isomerization of CNH_2^+ (4) to the thermochemically more stable $HCNH^+$ (2) isomer is prevented by a barrier as high as 150 kJ mol^{-1}. Schaefer, H. F., III *Acc. Chem. Res.* **1979**, *12*, 288.

(18) McLafferty, F. W.; McGilvery, D. C. *J. Am. Chem. Soc.* **1980**, *102*, 6189.

(19) We should like to draw the reader's attention to the remarkable similarity of the $CH_3N^{+\cdot}$ potential energy surface and that of the isoelectronic $CH_2O^{+\cdot}$ system; for the latter, see: DeFrees, D. J.; McLeon, A. D.; Herbst, C. *Astrophys. J.* **1984**, *279*, 322. See also: Bouma, W. J.; Burgers, P. C.; Holmes, J. L.; Radom, L. *J. Am. Chem. Soc.*, submitted for publication.