PERKIN 2

The retro-ene reaction of gaseous immonium ions revisited†

Theis I. Sølling*‡ and Steen Hammerum

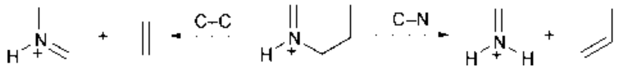
Department of Chemistry, University of Copenhagen, Universitetsparken 5,
DK 2100 Copenhagen, Denmark

Received (in Cambridge, UK) 19th June 2001, Accepted 10th October 2001
First published as an Advance Article on the web 9th November 2001

The retro-ene reaction is a common reaction of metastable immonium ions, leading to the expulsion of an alkene molecule. The kinetic energy release that accompanies this reaction decreases with alkyl substitution on the γ-carbon of the immonium ion. A number of authors have taken this result to indicate that the retro-ene reaction proceeds in a non-concerted manner *via* a carbocation intermediate. Using *ab initio* calculations to test this hypothesis we find that the retro-ene reaction is a concerted process, in which the reactant immonium ion is connected to the products *via* a single six-membered cyclic transition state. The calculated energy barriers and the measured kinetic energy releases are highly sensitive to alkyl substitution at the γ-position, which indicates that a substantial fraction of the positive charge of the transition state resides at the γ-carbon, not that the retro-ene reaction is a stepwise process with a carbocation intermediate.

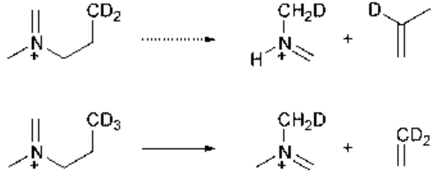
Introduction

The unimolecular reactions of gaseous immonium ions have been the focus of many investigations over the years,[1–13] and in particular Bowen's work has contributed significantly to the understanding of the unimolecular processes by which immonium ions decompose.[1–9,11] The two most common reactions lead to elimination of an alkene molecule by C–C or C–N cleavage (*e.g.* Scheme 1).[7]



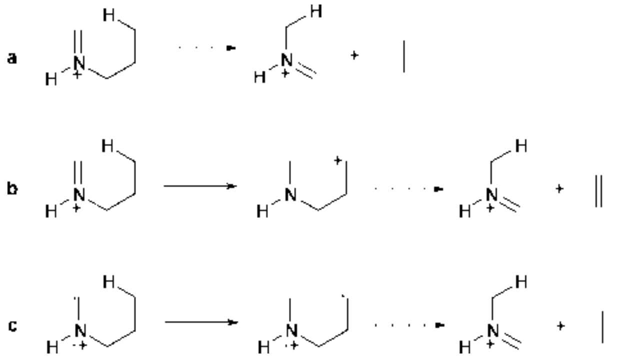
Scheme 1

The focus of this investigation is the C–C cleavage. This is a retro-ene reaction,[14] and we will refer to it as such. Studies of retro-ene reactions of deuterium labelled immonium ions (*e.g.* Scheme 2) show that the reaction proceeds with specific transfer of a γ-hydrogen;[7,9,10] this is uncommon for even-electron ions.[15]



Scheme 2

Several attempts have been made to clarify the details of the mechanism of alkene loss from immonium ions. The specific hydrogen transfer has reminded some authors of the McLafferty rearrangement, a process that takes place in odd-electron ions, but at least three different reaction mechanisms have been proposed (**a–c**, Scheme 3).[7,10,12]



Scheme 3

In the process depicted in Scheme 3a, a hydride ion is transferred in a six-membered cyclic transition state, and the C–C bond is broken concurrently. Bowen has argued against this mechanism in a series of papers.[1–9,11] The process in Scheme 3b is stepwise and involves the formation of an intermediate carbocation, which in a second step dissociates to the product alkene and immonium ion. Gross and Veith[10] find this mechanism to be in better agreement with the available experimental data, and Bowen and co-workers[1–9,11] also describe the retro-ene reaction of gaseous immonium ions in this manner. Another two-step mechanism (Scheme 3c) was proposed by Budzikiewicz and Bold.[12] The cationic intermediate is replaced by two bi-radicaloid species. Viewed this way the process is reminiscent of reactions in open-shell systems which often exhibit specific γ-hydrogen transfer. The disagreement with regard to the mechanism appears to be clear-cut; the present study is an attempt to distinguish between the three alternative descriptions with the aid of *ab initio* calculations and kinetic energy release measurements.

Experimental

Mass spectrometry

The immonium ions under study were formed by spontaneous loss of an alkyl radical from ionised alkyl amines.[16] The precursor alkyl amines were prepared by unexceptional methods

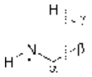
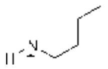
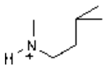
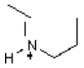
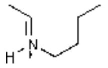
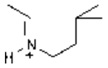
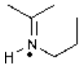
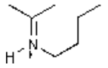
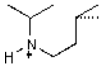
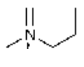
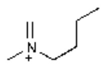
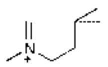
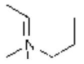
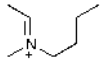
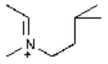
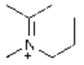
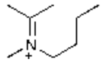
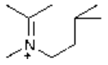
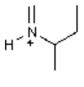
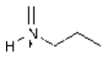
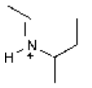
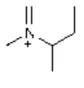
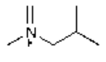
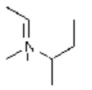
---

† Electronic supplementary information (ESI) available: Table s1 [G2(MP2) total energies of the involved species] and Table s2 [archive entries for MP2(full)/6-31G(d) optimised geometries]. See http://www.rsc.org/suppdata/p2/b1/b105386h

‡ *Present address*: Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125, USA.

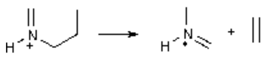
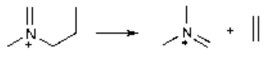
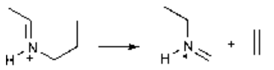
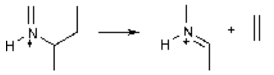
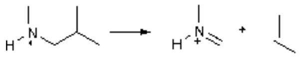
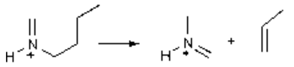
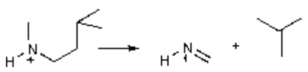
DOI: 10.1039/b105386h

Table 1 Kinetic energy releases ($T_{0.5}$) that accompany the retro-ene reaction of immonium ions†

Reactant	$T_{0.5}$	Reactant	$T_{0.5}$	Reactant	$T_{0.5}$
	65		32		3
	64		41		9
	[b]		46		18
	70		44		17
	70		51		33
	72		56		42
	80		52		[b]
	81		63		81

[a] Values in kJ mol^{-1}. [b] Does not decompose *via* the retro-ene reaction.

Table 2 Calculated energy barriers and reaction energies for the retro-ene reactions and binding energies of the exit-channel complexes‡

Reaction	E_0 [b]	E_{bind} [b]	E_r [b]
	166	22	112
	174	21	110
	197 [c]	22	143
	160 [d]	21	81
	161 [e]	33	115
	130 [f]	30	104
	99	40	100

[a] G2(MP2) values in kJ mol^{-1} at 0 K. [b] See Fig. 1. [c] Energy barrier for the decomposition of the *Z*-form of the reactant, the *E*-form energy barrier is 200 kJ mol^{-1}. [d] There is an energy barrier of 164 kJ mol^{-1} for the formation of the *Z*-*N*-methylethylideneimmonium ion. [e] CCCN angle in the reactant is approximately 60°. The reaction of the conformer with CCCN angles of 60° and 180° has an energy barrier of 168 kJ mol^{-1}. [f] CCCC angle in the reactant is approximately 60°. The reaction of the conformer with a CCCC angle of 180° has an energy barrier of 139 kJ mol^{-1}.

(usually by reduction of the appropriate amide or carbamate with $LiAlH_4$). The MIKE-spectra were recorded on a Jeol HX/HX110A four-sector mass spectrometer in three-sector mode under standard operating conditions. The kinetic energy releases were determined from the peak width at half height of the appropriate peaks in the MIKE spectrum measured under conditions of relatively high energy resolution and corrected for the small energy spread of the parent ion beam.

Computational methods

The thermochemical quantities were determined directly from total energies obtained with slightly modified versions of G2(MP2)[17] and G3(MP2),[18] in which the zero point vibrational energies were calculated at the MP2(full)/6-31(d) level and scaled by 0.9661.[19] This modification was introduced because the results of the geometry optimisation at the HF/6-31(d) and the MP2(full)/6-31(d) levels in some cases differ significantly. All first-order saddle points were characterised by the calculation of the vibrational frequencies (one imaginary frequency) and an intrinsic reaction coordinate (IRC) calculation. The quantum chemical calculations were carried out with the GAUSSIAN 94 and 98 suites of programs.[20,21] The calculated total energies are available as supporting data (Table s1), which also includes the MP2(full)/6-31G(d) optimised geometries in the form of GAUSSIAN archive entries (Table s2).†

Results and discussion

Kinetic energy releases ($T_{0.5}$)

Table 1 presents the kinetic energy release measured for the retro-ene reactions.

The first two sections of Table 1 demonstrate that the kinetic energy release decreases as the γ-carbon of the immonium ion becomes more substituted (*i.e.* along a row of Table 1). A similar comparison down a column shows that kinetic energy release increases slightly with the number of alkyl groups on the sp^2 carbon atom of the reactant. Further, the kinetic energy release increases when alkyl groups are introduced on the nitrogen atom (compare the columns of the first section with the corresponding columns of the second section). The third section of Table 1 illustrates the effect of alkyl substitution on the α- and the β-carbon atoms. The kinetic energy release increases significantly upon α substitution whereas it decreases slightly when the β-carbon becomes more substituted.

For reactions that involve carbocations as unstable intermediates, Hammond's postulate suggests that the transition states that are adjacent to the carbocation will resemble this species. Carbocations, and therefore also the adjacent transition states, are stabilised by alkyl substitution. Thus, the result of such a substitution is a decrease in the energy difference between the products and the transition state, at least when the final products are unaffected by alkyl substitution. Since the magnitude of the kinetic energy release is closely related to this energy difference, the observed variation of the kinetic energy release with the substitution on the γ-carbon has previously been taken to indicate that the retro-ene reaction is stepwise with an intermediate species with a cationic γ-carbon.[1–11] However, a concerted reaction involving a transition state with some cationic character at the γ-carbon would give rise to a similar relationship between the alkyl substitution at the γ-carbon and the kinetic energy release that accompanies the retro-ene reaction. To investigate this further, we carried out a series of calculations for representative retro-ene reactions.

Computational results

The seven immonium ions in Table 2 represent the possible alkyl substitutions on the *N*-propylmethylideneimmonium ion. In each case, our results indicate that only the concerted retro-ene reaction connects the reactant immonium ion with the products, an alkene and an immonium ion. A schematic presentation of the potential energy surface for this pathway is depicted in Fig. 1. We shall refer to the species that resides in the potential-energy well between the transition state and the separated products as an exit-channel complex. In all of the investigated cases it is composed of the product immonium ion and the product alkene molecule, and its presence is a

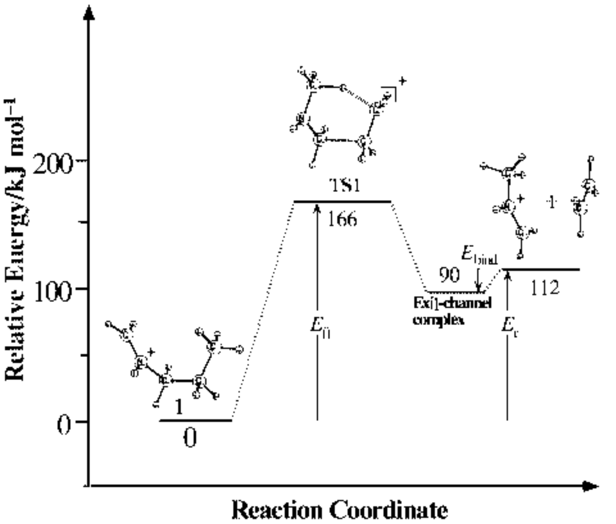


Fig. 1 Schematic energy profile for the concerted retro-ene reaction of gaseous immonium ions shown for $CH_3CH_2CH_2NH{=}CH_2^+ \longrightarrow C_2H_4 + CH_2{=}NHCH_3^+$.

natural consequence of ion–dipole and ion-induced–dipole interactions. Such species will always show up in detailed computational investigations, even though their actual presence will not always influence the experimental findings. We have tried to determine the geometry of $CH_3NHCH_2CH_2CH_2^+$-type ions in order to test the proposed intermediacy of carbocations. The results of a substantial number of attempts which involved various initial guess geometries for systems with either 0, 1 or 2 alkyl groups on the γ-carbon (to possibly induce a shift towards the stepwise mechanism) suggest that these species will always either dissociate without an energy barrier or undergo ring closure to form an azetidinium ion.

The calculated thermochemical quantities are presented in Table 2. The reaction energies are around 100 kJ mol^{-1}; the smaller reaction energy is found when the product immonium ion has an alkyl group on the sp^2 carbon whereas the larger reaction energy is found when the reactant immonium ion has an alkyl group on the sp^2 carbon. We have previously discussed how the difference between the stabilisation of immonium ions depends upon the substitution at the sp^2 carbon and the nitrogen, respectively.[22] The energies of the exit-channel complexes relative to the separated products increase with the number of carbon atoms in the alkene. This result is not surprising since the polarisability increases as the number of electrons increases. The calculated energy barriers (E_0) in Table 2 are strongly influenced by substitution at the γ-carbon.

Maccoll[23] has developed a scheme to estimate the heats of formation of carbocations. This scheme has previously been employed to assess the heats of formation of $CH_3NHCH_2CH_2CH_2^+$-type ions and thereby estimate a lower limit for the energy barriers of the corresponding retro-ene reaction involving a carbocation intermediate.[7,10] In this manner Gross and Veith[10] estimated that the propene loss from the *N*-butylmethylideneimmonium ion *via* an intermediate carbocation proceeds with a barrier of 331 kJ mol^{-1}. We calculate the barrier for the corresponding concerted process to be 140 kJ mol^{-1}. In the same manner Bowen[1,5,7,9] has estimated several energy barriers for retro-ene reactions, barriers that are significantly higher than the barriers we find for the corresponding concerted processes. For example, the barrier for ethylene loss from the *N*-propylmethylideneimmonium ion was estimated[1] to be 275 kJ mol^{-1}. We find the barrier for the corresponding concerted process to be 166 kJ mol^{-1}. This would seem to indicate that the mechanism involving an intermediate carbocation would require significantly higher energy than the concerted process.

The calculated geometries of the reactant immonium ions and the transition states are shown in Fig. 2. The distance in the transition state between the hydrogen atom under transfer and the γ-carbon is quite long, which shows that the hydrogen transfer is virtually complete in the transition state and therefore also that the cationic character at the γ-carbon is quite pronounced. The distance between the hydrogen under transfer and the γ-carbon increases with the number of alkyl substituents on the γ-carbon (from approximately 1.6 Å when the γ-carbon is primary to 1.9 Å when the γ-carbon is tertiary). Also, the breaking C–C bond becomes shorter as the number of alkyl groups on the γ-carbon increases. With no substituents (H-transfer from CH_3), the C–C bond length is 1.9 Å, this value reduces to 1.8 Å in the presence of one alkyl group; when two alkyl groups are attached to the γ-carbon the C–C bond length is only 1.7 Å. This shows that the transition state most closely resembles a carbocation when the reactant possesses a tertiary γ-carbon atom.

Concerted or two-step process?

The computational results provide direct evidence against a stepwise mechanism for the retro-ene reaction. Particularly, we note that the putative carbocation intermediate proposed in previous work[1–11] does not correspond to a stationary point. This is the case regardless of the degree of substitution at the γ-carbon, indicating that there is no change of mechanism when the hypothetical intermediate would have been stabilised by substitution. Also, the energy barriers estimated under the assumption that the reaction proceeds *via* an intermediate carbocation[1,5,7,9,10] are significantly higher than the energy barriers for decomposition *via* the concerted process.

The results of the kinetic energy release measurements agree with the results of the *ab initio* calculations. The reverse barrier (and therefore also the kinetic energy release) decreases as the number of alkyl groups on the γ-carbon atom increases. This is because the hydrogen transfer is virtually complete in the transition state for the concerted retro-ene reaction, which causes the charge density to be high on the transition state γ-carbon and lowers the transition-state energy when the number of alkyl groups on the γ-carbon increases. In fact, all calculated reverse barriers and experimentally determined kinetic energy releases are influenced in the same manner by the various alkyl substitutions that we have examined. The plot in Fig. 3 of $T_{0.5}$ *versus* the calculated barrier for the reverse reaction indicates proportionality between the two quantities ($R^2 = 0.98$). This is to some extent fortuitous because $T_{0.5}$ is influenced by many parameters in addition to the reverse barrier. However, for systems as similar as those in Table 1 it seems likely that these additional parameters would influence the kinetic energy release in a systematic manner if the mechanisms of decomposition are similar. The observed correlation in turn corroborates the assumption that there is a single decomposition channel, the concurrent γ-hydrogen transfer and C–C bond cleavage.

Peak shapes

The metastable peaks that are associated with the retro-ene reaction become broader, and eventually dish-shaped, as the size of the expelled alkene molecule decreases. This was noticed previously by Gross and Veith.[10] The width and shape of metastable peaks reflect not only the release of kinetic energy that accompanies a certain reaction, but also the distribution of the internal energy over the available degrees of freedom. A dish-shaped metastable peak is generally taken to indicate that the internal energy is distributed non-statistically amongst the reaction coordinate and the remaining $3N - 7$ degrees of freedom. For the retro-ene reaction, the observed variation in peak shape could be introduced by the presence of an exit-channel complex (Fig. 1). The lifetime of these complexes is determined by the energy barrier for the forward reaction (dissociation to yield the

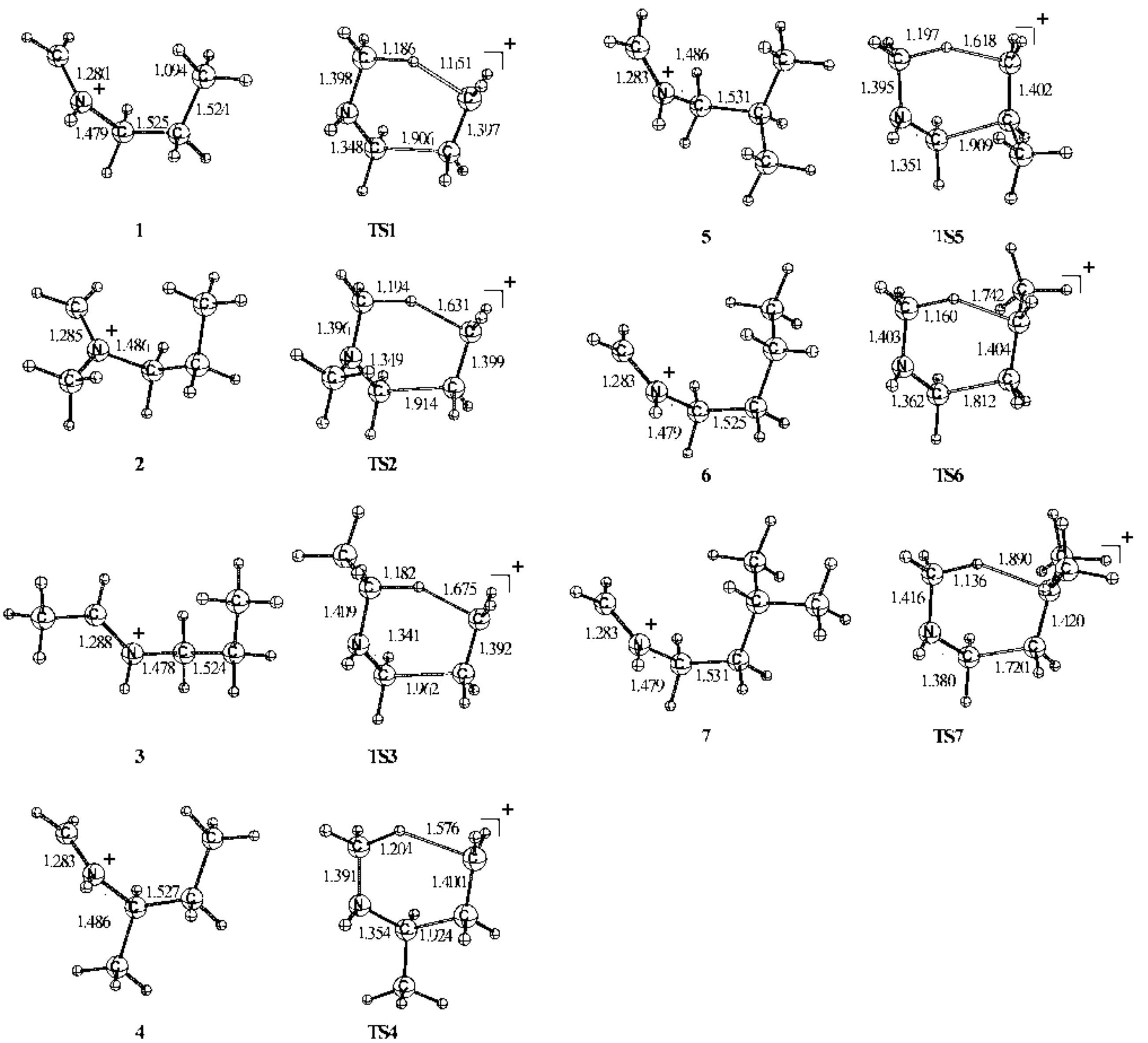


Fig. 2 Calculated geometries (MP2(full)/6-31G(d)) of the reactant immonium ions and transition states involved in the retro-ene reaction (bond lengths in Å; all the molecules under study have C_1 symmetry).

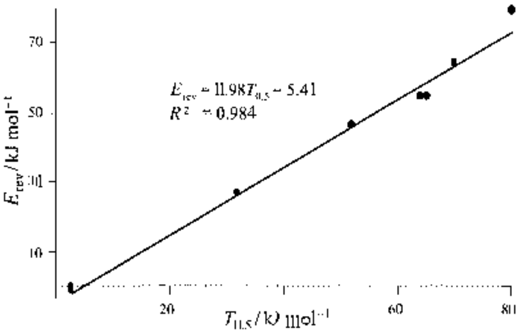


Fig. 3 Plot of the kinetic energy releases *versus* the calculated barriers for the reverse reaction (*i.e.*, the addition of an alkene to an immonium ion).

final products) and for the reverse reaction (the association to re-form the reactant immonium ion). The barrier towards dissociation of the exit-channel complex is smaller for smaller alkenes as the binding energy of the complex is smaller, and in turn the lifetime decreases. Therefore the energy randomisation is less efficient when the complex binding energy is small, *i.e.*, when a small alkene is expelled, which in turn results in a dish-shaped metastable peak.

Triplet mechanism

The mechanism proposed by Budzikiewicz and Bold[12] for the retro-ene reaction involves a species with two adjacent unpaired electrons which may represent an open-shell singlet immonium ion or an immonium ion excited to a triplet state. We have investigated the energetics for both types of species; the methylideneimmonium ion ($CH_2{=}NH_2^+$) was used as a model system.

The geometry of the lower-energy open-shell singlet of the methylideneimmonium ion ($^1A_2$) is shown in Fig. 4 along with the geometry of the methylideneimmonium ion in the ground state ($^1A_1$). The open-shell singlet is a first-order saddle point, which suggests that it would not be a proper intermediate in the retro-ene reaction. G3(MP2) calculations indicate that the open-shell singlet is 341 kJ mol^{-1} higher in energy than the closed-shell species. It would in turn appear unlikely that an open-shell singlet species is involved in the retro-ene reaction. The expectation value of the squared spin-projection operator ($\langle \boldsymbol{S}^2 \rangle$) of the open-shell methylideneimmonium ion is 1.035, indicating that a multi-reference wave function is required to describe the system properly and hence to obtain accurate energies. A similar observation was made for twisted ethylene which is isoelectronic with the twisted methylideneimmonium ion.[24] Twisted ethylene has been studied using both the G3(MP2)

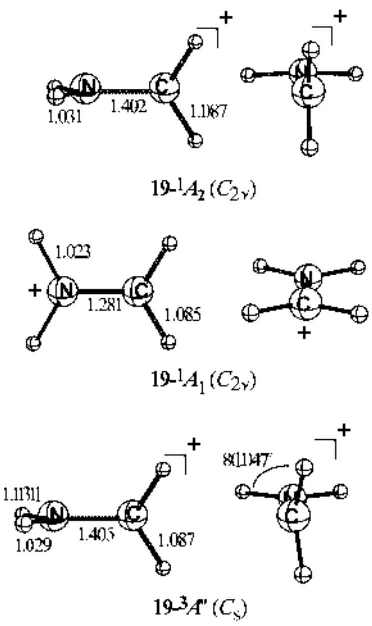


Fig. 4 Calculated geometries (MP2(full)/6-31G(d)) of the methylideneimmonium ion in the $^1A_2$, $^1A_1$ and $^3A''$ electronic states (bond lengths in Å).

method and the corresponding multi-reference procedure; the same value for the energy of twisted ethylene relative to ethylene in its ground state was obtained in either case.[24] The value reproduces that determined by experiment quite well.

The geometry of the methylideneimmonium ion in its lowest-lying triplet state ($^3A''$) is also shown in Fig. 4. The G3(MP2) heat of formation of this species is 335 kJ mol^{-1} higher than that of the ground-state $CH_2{=}NH_2{}^+$, which indicates that the energy of a triplet immonium ion is much too high for this species to be considered as intermediate in the retro-ene reaction.

Conclusion

The computational results indicate that the retro-ene reaction of gaseous immonium ions proceeds in a concerted manner. The hydrogen transfer is virtually complete in the transition state whereas the C–C bond is not entirely broken. The charge density at the γ-carbon atom is high in the transition state, and the reaction therefore shows pronounced sensitivity towards alkyl substitution at this site. This sensitivity is particularly evident from the result that introduction of γ-alkyl substituents induces large variations in the kinetic energy release that accompanies the retro-ene reaction.

Acknowledgements

We gratefully acknowledge Statens Naturvidenskabelige Forskningsraad and the Australian National University Supercomputing Facility for generous grants of computer time.

References

1 R. D. Bowen, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1219.
2 R. D. Bowen and A. G. Harrison, *Org. Mass Spectrom.*, 1981, **16**, 180.
3 R. D. Bowen, *J. Chem. Soc., Perkin Trans. 2*, 1982, 403.
4 R. D. Bowen, *J. Chem. Soc., Perkin Trans. 2*, 1982, 409.
5 R. D. Bowen, *J. Chem. Soc., Perkin Trans. 2*, 1989, 913.
6 R. D. Bowen, A. W. Colburn and P. J. Derrick, *Org. Mass Spectrom.*, 1990, **25**, 509.
7 R. D. Bowen, *Mass Spectrom. Rev.*, 1991, **10**, 225.
8 R. D. Bowen, A.W. Colburn and P. J. Derrick, *J. Chem. Soc., Perkin Trans. 2*, 1993, 285.
9 R. D. Bowen, A. W. Colburn and P. J. Derrick, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2363.
10 J. H. Gross and H. H. Veith, *Org. Mass Spectrom.*, 1993, **28**, 867.
11 R. D. Bowen, *Org. Mass Spectrom.*, 1993, **28**, 1577.
12 H. Budzikiewicz and P. Bold, *Org. Mass Spectrom.*, 1991, **26**, 709.
13 K. Levsen and F. W. McLafferty, *J. Am. Chem. Soc.*, 1989, **111**, 3987.
14 H. M. R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 556.
15 M. Zollinger and J. Seibl, *Org. Mass Spectrom.*, 1985, **20**, 649.
16 F. W. McLafferty and F. Tureček, *Interpretation of Mass Spectra*, 2nd edn., University Science Books, Mill Valley, 1983.
17 L. A. Curtiss, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, 1995, **103**, 4192.
18 L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov and J. A. Pople, *J. Chem. Phys.*, 1999, **110**, 4703.
19 A. P. Scott and L. Radom, *J. Phys. Chem.*, 1996, **100**, 16502.
20 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, GAUSSIAN 94 (rev. E.2), Gaussian Inc.: Pittsburgh, PA.
21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, S. J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98 (rev. A.7), Gaussian, Inc.: Pittsburgh, PA, 1998.
22 S. Hammerum and T. I. Sølling, *J. Am. Chem. Soc.*, 1999, **121**, 6002.
23 A. Maccoll, *Org. Mass Spectrom.*, 1985, **20**, 715.
24 T. I. Sølling, D. M. Smith, L. Radom, M. A. Freitag and M. S. Gordon *J. Chem. Phys.*, in the press.