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Primary Event in the Thermal Dehydrochlorination of Pristine Poly(vinyl chloride): Intermediacy of a Cyclic Chloronium Ion

Krishnan Raghavachari,* Robert C. Haddon,* and William H. Starnes, Jr.

Contribution from the Bell Laboratories, Murray Hill, New Jersey 07974.

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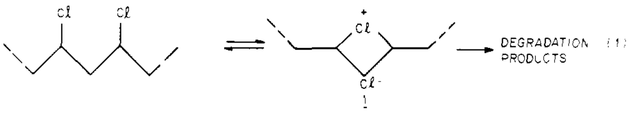
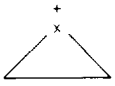
Abstract: Ab initio molecular orbital theory has been used to assess the stabilities of the bridged and open forms of the haloethyl and halopropyl cations. The introduction of polarization functions and the effects of electron correlation into the calculations is found to be mandatory in order to obtain a balanced description of the systems. The results provide strong support for the intermediacy of a cyclic chloronium ion in the thermal degradation of pristine poly(vinyl chloride).

The mechanism of the nonoxidative thermal dehydrochlorination of poly(vinyl chloride) (PVC) has been the subject of considerable attention.[1] It is known that the degradation process is autocatalytic and that once initiated it proceeds with great rapidity.[1] This is ascribed to a "zipper" mechanism whereby the generation of unsaturation facilitates the elimination of hydrogen chloride,[1] probably via the intermediacy of conjugated polyenyl cations.[1a,2] However, the primary event in the degradation of the pristine portion of PVC (the portion containing no structural defects such as unsaturation, branches, etc.[1]) is less well understood, although recent experimental[1a,3] and theoretical[1a,3] studies strongly suggest the formation of a cyclic chloronium ion (**1**, eq 1) to be the critical step, at least under some conditions. In order to assess the viability of this process, we have carried out a detailed theoretical study of a number of model systems.

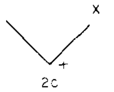


There is a long history of interest in haloalkyl cations, beginning with the original proposal of a bridged bromonium ion[4] (**2b**, X = Br). Strong experimental evidence is now available for the existence of the cyclic halonium ions **2b** (X = Cl, Br, I), **4b** (X = Cl, Br, I), and **5b** (X = Cl, Br, I), either as the parent compounds or as alkylated derivatives in nonnucleophilic media.[5] In the gas phase, it has been shown[6] that for X = Cl, **2c** is preferred over **2b** by 5.6 kcal/mol, whereas for X = Br, **2b** is more stable than **2c** by 1.4 kcal/mol. The theoretical studies on **2** (X = F, Cl), **4** (X = Cl), and **5** (X = Cl) have generally favored the bridged ion (**b**) over the open ion (**a**), although the distinction is less clear-cut for X = F.[7] We have included **2** in our study in order to make contact with other theoretical work in the area of halonium ion chemistry.

2a

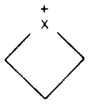


2b



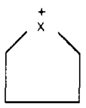
2c

3a



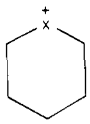
3b

4a



4b

5a



5b

The principal subject of the present paper (**3**) has been studied much less extensively, and we are not aware of any previous theoretical calculations on this system, except for those performed in these laboratories and described in earlier publications.[1a,3] Experimental evidence for the existence of **3b** (X = Cl, Br, I) or its derivatives[1a,3,8] is not abundant either, but as noted above, there are strong indications for the formation of **3b** (X = Cl) structures from PVC and related substrates.[1a,3] Intervention of a **3b** (X = Cl) structure also seems to be required in order to account for the occurrence of a minor amount of 1,3 chlorine migration during the trifluoroacetolysis of 3-chloro-1-butyl triflate.[8a,b] Analogous halogen shifts have provided indications for the incursion of **3b** intermediates (X = Br,[8a-e] I[8b]) in other reactions as well, but the only report of a stable **3b** (X = halogen) structure seems to be that of Exner et al.,[8f] who obtained strong ^{1}H NMR evidence for the existence of a **3b** (X = Br) species in SbF_5–SO_2ClF solution at low temperatures.

The conformations considered in detail in the present study are shown in Figure 1; structures **6a** and **7a** are the eclipsed forms of the 2-haloethyl cations, and **6b** and **7b** are the corresponding three-membered rings with the bridging halogen. Structures **8** and **9** represent the open and bridged structures of the halopropyl cations, whereas **10** corresponds to the 2,4-dimethyl-substituted forms of **9**, which are more representative of the intermediate (**1**) that is thought to be involved in the degradation of PVC. The two conformation **10b** and **10c**, with symmetries C_s and C_2, respectively, were considered for the bridged form of **10**.

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Table I. Negative of the Total Energies at the HF/STO-3G Optimized Geometries (Hartrees)

	HF				MP2			MP3
mol	STO-3G	6-31G	6-31G + D	6-31G*	6-31G	6-31G + D	6-31G*	6-31G*
6a	174.84083	177.06687	177.08932	177.12839	177.34567	177.42235	177.52665	177.54783
6b	174.87215	177.04712	177.08113	177.12148	177.34176	177.43159	177.53791	177.55382
7a	531.37945	537.12712	537.14867	537.18360	537.32928	537.43680	537.54230	537.57637
7b	531.40978	537.13866	537.16567	537.20827	537.35842	537.47339	537.58816	537.61751
8a	213.43361	216.11081	216.13056	216.18415	216.47809	216.55331	216.71245	
8b	213.51159	216.10795	216.13484	216.19049	216.48377	216.56978	216.73203	
9a	569.97689	576.16300	576.18297	576.23331	576.45562	576.56348	576.72398	
9b	570.02469	576.17108	576.19725	576.25306	576.47758	576.59393	576.76227	
10a	647.18597	654.24822	654.26655		654.72440	654.83189		
10b	647.21605	654.24207	654.26378		654.73299	654.84682		
10c	647.21549							

Computational Methods

Four basis sets were employed within the framework of the Hartree–Fock (HF) method, which was used as the starting point throughout this work. The minimal STO-3G[9] basis was used to obtain all the geometries of systems **6**–**10**. The energies at these geometries were then evaluated with the split-valence 6-31G basis,[10,11] the 6-31G + D basis,[11,12] which has polarization (six d type) functions on the halogen (exponent 0.8 and F and 0.75 on Cl), and the 6-31G* basis,[11,12] which also has polarization functions on carbon. Electron correlation effects were included in all cases by the Moller-Plesset (MP) perturbation treatment[13] at the second-order (MP2) level of theory.[14] The effect of the third-order[15] (MP3) correction was evaluated with the 6-31G* basis set on the smaller systems **6** and **7**, and this contribution was added to the MP2 results for **8**, **9**, and **10** to give projected third-order results for these systems. For the largest system, **10**, calculations were performed only up to the 6-31G + D level (84 basis functions), the effect of the 6-31G* basis for this system being obtained by extrapolation of the results obtained for **9**.

Results and Discussion

The geometries for all of the systems considered were completely optimized within the given symmetry constraint with the STO-3G basis; for **10a** this represents the optimization of all of the 42 geometrical parameters. Some of the interesting geometrical parameters involved in the skeletons of these systems are shown in Figure 1.

To consider the effect of larger basis sets on the geometries of these systems, the structures of **6a** and **6b** were optimized with the larger 6-31G* basis. (Optimized total energies were −177.13552 and −177.12763 Hartrees, respectively.) The calculated relative energy, Δ = [open (**a**) − bridged (**b**)] = −4.9 kcal/mol, is very close to the Δ calculated with the 6-31G* basis and the STO-3G geometry (−4.3 kcal/mol). Hence the effects of larger basis sets on the geometries of the other systems were not considered.

The optimized STO-3G geometries were then used in single-point computations with the larger 6-31G, 6-31G + D, and 6-31G* basis sets. Electron correlation was included at the MP2 or MP3 level in these computations. The use of such progressively larger basis sets is useful in order to achieve a proper understanding of the various basis-set effects involved. The calculated total and relative energies are listed in Tables I and II, respectively. In the bridged form of **10**, the C_s structure **10b** was found to be slightly more stable (by ca. 0.4 kcal/mol) than the C_2 structure **10c** in the STO-3G optimization, and **10c** was thus not considered in further computations.

The haloethyl cation systems **6** and **7** have been the subject of investigations by Hehre and Hiberty,[7c] Hopkinson et al.,[7d,e] and Lischka and Kohler.[7f] Of these studies, only the work of Lischka and Kohler[7f] involved computations with the inclusion of electron correlation. These workers employed a double ζ plus polarization basis and electron correlation by an approximate CEPA method, and they found the bridged form to be more stable in both **6** and **7** by 1.4 and 30.0 kcal/mol, respectively.

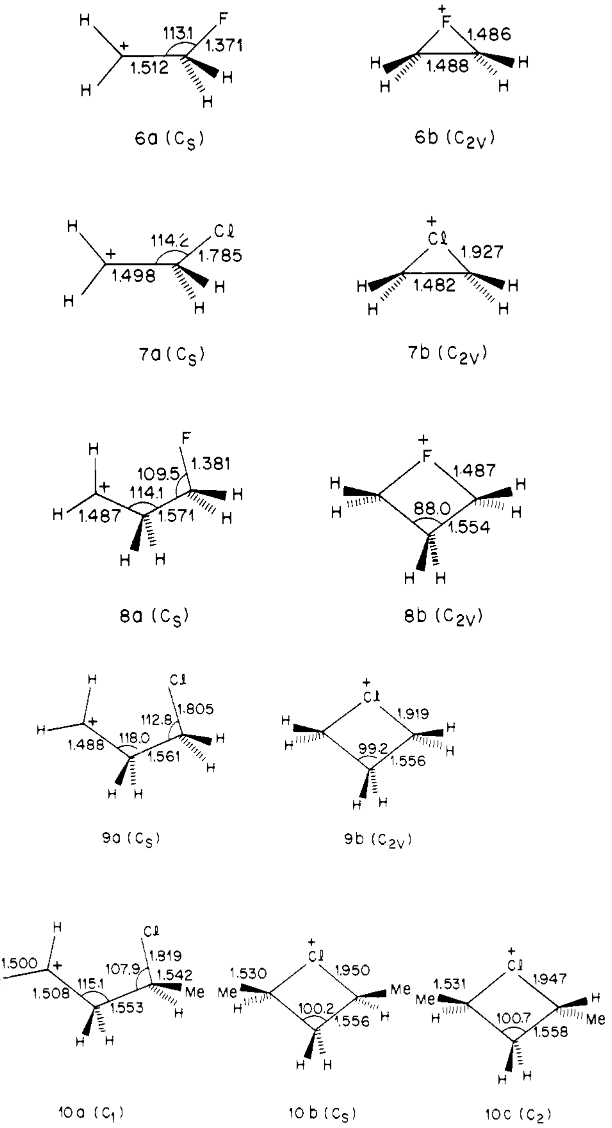

Figure 1. Conformations of the model systems considered in this study. Bond lengths are in angstroms and bond angles are in degrees.

Our results on **6** and **7** are similar to the earlier observations. At the HF level with the 6-31G* basis (HF/6-31G* level), the open form **6a** was found to be more stable than the bridged form **6b** by 4.3 kcal/mol. It has been shown before[16] that HF theory

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Table II. Relative Energies, Δ[a] (kcal/mol)[b]

	HF				MP2			MP3
structure	STO-3G	6-31G	6-31G + D	6-31G*	6-31G	6-31G + D	6-31G*	6-31G*
6	19.7	−12.4	−5.1	−4.3	−2.5	5.8	7.1	3.8
7	19.0	7.2	10.7	15.5	18.3	23.0	28.8	25.8
8	48.9	−1.8	2.7	4.0	3.6	10.3	12.3	(9.0)
9	30.0	5.1	9.0	12.4	13.8	19.1	24.0	(21.0)
10	18.9	−3.9	−1.7	(1.7)	5.4	9.4	(14.3)	(11.3)

[a] Δ = [open (a) − bridged (b)]. [b] Values in parentheses are projected estimates.

Table III. Effect of Basis Sets and Electron Correlation on Relative Energies, Δ[a] (kcal/mol)

	HF			6-31G*	
structure	Δ(6-31G) − Δ(STO-3G)	Δ(6-31G + D) − Δ(6-31G)	Δ(6-31G*) − Δ(6-31G + D)	Δ(MP2) − Δ(HF)	Δ(MP3) − Δ(MP2)
6	−32.1	7.3	0.8	11.4	−3.3
7	−11.8	3.5	4.8	13.3	−3.0
8	−50.7	4.5	1.3	8.3	
9	−24.9	3.9	3.4	11.6	
10	−22.8	2.2			

[a] Δ = [open (a) − bridged (b)].

favors the open form and the electron correlation is important in correctly describing the bridged form. All the previous calculations on **6** favor the classical form at the HF level. When electron correlation is included at the MP2 level, the order of stability is reversed, and the bridged form **6b** is now found to be more stable by 7.1 kcal/mol. The inclusion of third-order perturbation moderates this result somewhat, and the bridged form is then 3.8 kcal/mol more stable than the open form **6a**. This effect of MP2 in overestimating the correlation corrections has also been previously noted.[16]

In the case of the chloronium ions **7**, the bridged form **7b** is more stable than **7a** even at the HF level, and at the HF/6-31G* level, **7b** is lower in energy by 15.5 kcal/mol. This result is in qualitative agreement with all the previous computations. Inclusion of electron correlation favors the bridged form further, and at the final MP3/6-31G* level, **7b** is 25.8 kcal/mol more stable than **7a**. The MP2 overshoot of the effect of correlation is seen here also.

Our calculated energy differences, Δ, of 3.8 and 25.8 kcal/mol for **6** and **7**, respectively, are still slightly different from Lischka and Kohler's[7f] values of 1.4 and 30.0 kcal/mol. Part of this difference stems from the different basis sets used in the two studies. The remaining difference is probably due to the approximate nature of the CEPA calculations employed by Lischka and Kohler.

The halopropyl system has not been studied previously in other laboratories. In the case of the fluoropropyl system **8**, even at the HF/6-31G* level the bridged form **8b** is more stable than **8a** by 4.0 kcal/mol. This ordering is the reverse of that found for the fluoroethyl system **6**. Electron correlation favors the bridged form further, and at the projected MP3/6-31G* level, the bridged form is 9.0 kcal/mol lower in energy.

The chloropropyl system **9** is important in determining the stability of **1**, and its behavior is found to be very similar to that of the chloroethyl system **7**. At the HF/6-31G* level, the bridged form **9b** is lower in energy by 12.4 kcal/mol. Electron correlation increases its stability further, and at the projected MP3/6-31G* level, it is 21.0 kcal/mol more stable than the open form **9a**.

Even though **9** has the local structure necessary to provide a model for **1**, there is a major difference at the 2,4-positions. In order to mimic more closely the situation in **1**, side chains should be attached to **9**, and this has been accomplished by means of methyl group substitutions, which lead to the structure **10**. It has been previously demonstrated[1a,3] that the substitution of larger groups than methyl makes little difference to the relative energies in this system.

The stability of the open form is enhanced significantly in **10**. The relative energy Δ is now reduced to 1.7 kcal/mol at the projected HF/6-31G* level, a result that may be compared to the HF/6-31G* value of 12.4 kcal/mol in **9**. The major difference between the two systems is the nature of the carbocation involved in the open form. In the case of **9a** there is a primary carbenium ion, whereas **10a** has a secondary carbenium ion with a much higher stability.

The introduction of electron correlation improves the stability of the bridged form **10b** considerably, and at the projected MP3/6-31G* level, it is 11.3 kcal/mol more stable than the open form **10a**. It should be remembered that the effect of the 6-31G* basis has been taken from **9** in this projection, but this assumption is expected to be reliable to within 2 kcal/mol.

Before the implications of this result are considered, it is illustrative to consider the various terms that contribute to the energy difference Δ. Table III contains the breakdown of the basis set and correlation energy contributions to Δ, and all the compounds **6–10** may be considered together in this analysis. As the basis set is increased from the minimal STO-3G to the extended 6-31G, the open form is stabilized in all cases. The stabilization ranges from 11.8 kcal/mol in the case of chloroethyl system **7** to 50.7 kcal/mol in the case of fluoropropyl system **8**. In the case of **9** and **10**, which are of primary importance in this study, the stabilization is about 23–25 kcal/mol. As the basis set is made larger by the introduction of d-type polarization functions, the bridged form is stabilized. The stabilization on going from 6-31G to 6-31G* ranges from 5.8 kcal/mol in the case of **8** to 8.3 kcal/mol in the case of **7**. The 6-31G + D results are always intermediate between 6-31G and 6-31G*. Inclusion of electron correlation is very important in determing the relative stability Δ, as correlation always favors the bridged form. The contribution of d functions and correlations to the stability of the bridged form has been noted previously in the vinyl and ethyl cations.[16] The stabilization from correlation at the MP2 level ranges from 8.3 to 13.3 kcal/mol; however, this stabilization is moderated to the extent of about 3 kcal/mol by the third-order perturbation correction (MP3).

It can seen from this analysis that both d-type polarization functions and electron correlation must be included in order to obtain a reliable estimate of the energy difference between the open and bridged forms of the cations studied here. Even though this observation has been pointed out previously in the case of carbocations, its importance cannot be overemphasized.

The results of this study allow us to conclude that structure **1** is, indeed, a viable intermediate in the thermal degradation of PVC and in related reactions. Further experimental evidence pertaining to this problem will be discussed at a later time.[17]

Registry No. Poly(vinyl chloride), 9002-86-2.

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(17) Starnes, W. H., Jr. et al., to be published.