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# ON THE INTERMEDIACY OF TRIMETHYLENECHLORONIUM IONS

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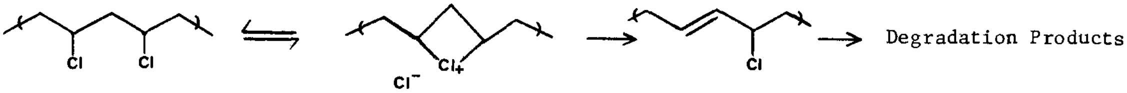
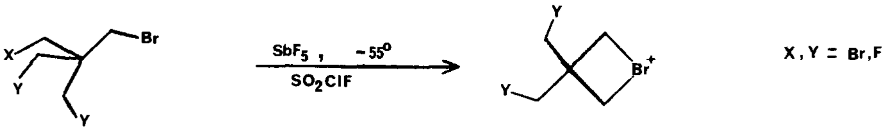
Summary. Semiempirical SCF MO calculations are presented which predict that α, α, α´, α´-tetraalkylethylenechloronium and trimethylenechloronium ions are more stable than some experimentally observed ions with larger ring sizes.

Catalyzed and uncatalyzed poly(vinyl chloride) (PVC) decomposition has been the subject of many recent investigations.[1-5] The purely thermal degradation of PVC is autocatalytic and is known to initially proceed to polyene degradation products with the probable intermediacy of polyenyl cations.[1-4] The initiating event is not known but recent experimental[1,4b] and theoretical[1,4b,5] studies suggest neighboring chlorine participation leading to the trimethylenechloronium ion as an intermediate (Scheme 1).



Scheme 1

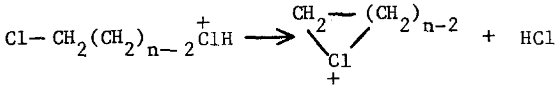
Trimethylenechloronium ions are especially interesting species because they are virtually unknown experimentally.[6a,7] Indeed, their elusiveness, in part, prompted the proposal of a bonding theory which explained their unusual instability.[8] The preparation of destabilized long-lived four-membered ring halonium ions by Exner et. al.[9] (Scheme 2) and subsequent understanding of rearrangement processes in cyclic halonium ions[10] has given these ions rebirth.



Scheme 2

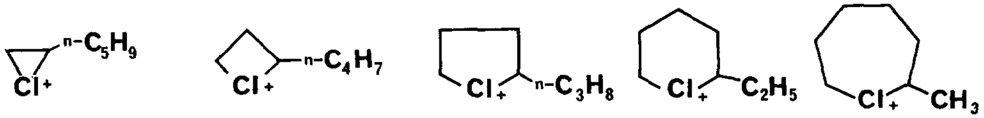
Several years ago we began a theoretical study of cyclic halonium ion-chloroalkyl carbocation processes in order to gain insight into some reactions observed in solution. Those studies,[11] which utilized the MINDO/3 SCF MO method,[12] agreed quite well with experiment.[13] Our MINDO/3 computations of the smaller halonium ion ring systems were limited pending our evaluation of the method's applicability. Subsequently, we have rather thoroughly evaluated the MINDO/3 method investigating ring size[14] and branching[15] errors and the applicability of the method to chloronium ions,[16] carbocations,[17] and various heteroatom systems.[18] MINDO/3 is the current method of choice for general mechanistic work with chloronium ions[16] and carbocations.[16,17] Therefore, in view of the recent theoretical treatment of trimethylenechloronium ions,[5] our theoretical studies related to the stability of cyclic chloronium ions are presented.

We have employed three types of MINDO/3 computations to gain insight into the relative stability of cyclic chloronium ions. The first is the ring closure reaction defined by eq. (1). The relative $\Delta H_{reac}$ for the conversions[19] are respectively, 20.6, 18.8, 2.0, (0) and (0) kcal/mole for the three to seven-membered rings (n = 3 to n = 7, eq. 1). This order is not unexpected based on considerations of strain and electronic effects. Thus, ring strain and their greater relative need for HCl solvation[20] cause the systems where n = 3 and 4 to greatly prefer the noncyclic form.



$$Cl-CH_2(CH_2)_{n-2}\overset{+}{Cl}H \longrightarrow \underset{\underset{+}{Cl}}{CH_2-(CH_2)_{n-2}} + HCl \qquad (1)$$

In solution studies under stable ion conditions, it has been found that α,ω-dihalides often cyclize with rearrangement.[6,10] For example, 1,7-dibromoheptane and apparently 1,7-dichloroheptane initially cyclize to the six-membered rather than the seven- or eight-membered rings apparently with hydride shifts preceding cyclization.[10a,d] Based on previous results, calculated energies[19] of the cyclic gas phase ions resulting from sequential hydride shifts (following ionization of 1,7-dichloroheptane) should parallel results in non-nucleophilic media.[10d,16,20] The results are shown below. The pattern is similar to that for the unsubstituted ions except that the three-membered ring seems to have become relatively more stable than the four-membered ring. We believe that this is an artifact.



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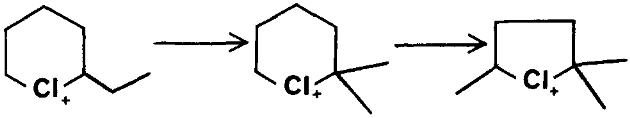
|---|---|---|---|---|---|
| MINDO/3[19,21] rel $\Delta H_f$ (kcal/mole) | 11.5 | 17.4 | 2.4 | (0) | 0.3 |

For the above systems in solution, it is further observed that the six-membered rings may rearrange to more-substituted five-membered rings.[10] This is especially true with chloronium ions where the process shown in eq (2) is implicated.[10,21] The MINDO/3 calculated gas phase $\Delta H_f$s

$$Cl(CH_2)_7Cl \xrightarrow[SO_2,\ -40°]{SbF_5}$$

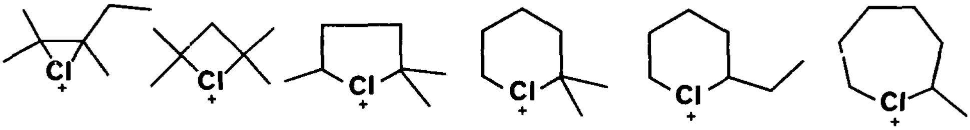


(2)

| MINDO/3[19,21] $\Delta H_f$ (kcal/mole) | 137.3 | 122.7 | 114.0 |
|---|---|---|---|

for the three ions show why this rearrangement route is so facile. This also further demonstrates the powerful stabilizing effect of alkyl groups at the α-carbons of chloronium ions.[10,11,16]

A comparison of the ions from eq. (2) with cyclic isomers having three-, four- and seven-members is especially interesting in light of the renewed interest in the four-membered ring system. The MINDO/3 energies,[19,22] shown below, reflect a dramatic energy shift from the unsubstituted and monosubstituted ions discussed above. Clearly the substitution pattern can be more important than ring size in influencing ring stability.



| | | | | | | |
|---|---|---|---|---|---|---|
| MINDO/3[19,21] $\Delta H_f$ (kcal/mole) | 102.0 | 105.5 | 114.0 | 122.7 | 137.3 | 137.6 |
| rel energies | (0) | 3.5 | 12.0 | 20.7 | 35.3 | 35.6 |

Earlier attempts to prepare stable four-membered cyclic halonium ions were carried out with precursors which would give low degrees of ring substitution at the α-positions. Thus, in light of these studies, the failure to obtain stable four-membered ions is not surprising. Exner et. al.[9] apparently succeeded because their ions would rearrange only to less stable species. We presently are seeking experimental verification of these studies by attempting synthesis of four-membered halonium ions which will exist in equilibrium with ring-opened carbocations.[7,10]

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(22) Branching errors have been applied as recommended in ref. 15.

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