Gas Phase Isomerisation of Saturated C_6 and C_8 Primary, Secondary, and Tertiary Carbonium Ions

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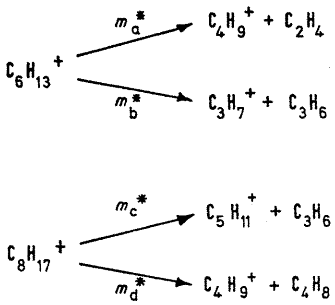
Summary Saturated C_8^+ and C_8^+ carbon ions, generated from primary, secondary, and tertiary bromides or iodides by electron impact, isomerize to a common structure (or structures) prior to reaction *via* olefin elimination after a lifetime of a few μsec.

SATURATED alkyl carbonium ions can be generated conveniently in the gas phase by loss of a bromine or iodine radical from the compounds $C_nH_{2n+1}Br$ or $C_nH_{2n+1}I$ upon electron impact. We have used this technique to generate $C_4H_9^+$ cations from primary, secondary, and tertiary halides and have shown that such cations are isomerized to a common structure or structures prior to further reaction *via* metastable transitions.[1] We now show that this behaviour is also exhibited by the higher C_6 and C_8 saturated alkyl carbonium ions.

The ions $C_6H_{13}^+$ and $C_8H_{17}^+$ were chosen for study since both undergo *competitive* eliminations of neutral olefins in metastable transitions,[2,3] as follows:



Metastable transitions arise from ions having a relatively narrow band of energies only slightly in excess of the energy of activation for reaction. If two reactions compete to the same extent within this narrow band of energies when the decomposing ion is generated from different precursors, then it may be concluded that the ions undergoing metastable transitions have a common structure, or structures.[2,4] The data given in Tables 1 and 2 summarize competing metastable transitions undergone by $C_6H_{13}^+$ and $C_8H_{17}^+$ carbonium ions, generated from primary, secondary, and tertiary bromides and iodides. The relative abundances given refer to reaction occurring in the first field-free region of an AEI MS9 double-focussing mass spectrometer at electron beam energies of 15, 20, and 70 ev.

TABLE 1

Ratio $[m_b^*]/[m_a^*]$ *of competing metastable transitions undergone by* $C_6H_{13}^+$ *ions*

		$[m_b^*]/[m_a^*]$†	
Parent compound	15 ev	20 ev	70 ev
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2I$	1·58	1·60	1·61
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$	1·60	1·60	1·62
$(CH_3)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2I$	1·56	1·58	1·61
$(CH_3)_2{\cdot}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$	1·58	1·58	1·60
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$	1·60	1·60	1·61
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$	1·55	1·60	1·60
$(CH_3)_2CH{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$	1·60	1·58	1·62
$(CH_3)_2CH{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$	1·55	1·58	1·60
$CH_3{\cdot}CH_2{\cdot}CH_2C(CH_3)_2I$	1·6	1·6	1·6
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}C(CH_3)_2Br$	1·6	1·6	1·6

TABLE 2

Ratio $[m_d^*]/[m_c^*]$ *of competing metastable transitions undergone by* $C_8H_{17}^+$ *ions*

		$[m_d]/[m_c]$†	
Parent compound	15 ev	20 ev	70 ev
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2I$	1·48	1·48	1·50
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br$	1·50	1·48	1·51
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHI{\cdot}CH_3$	1·49	1·50	1·52
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CH_3$	1·46	1·48	1·50
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CI(CH_3)_2$	1·5	1·5	1·5
$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CBr(CH_3)_2$	1·5	1·5	1·5

† Standard deviations for the quoted ratios are $\pm 0{\cdot}05$ for the primary and secondary halides, and $\pm 0{\cdot}3$ for the tertiary halides.

The ratios of metastable peak abundances are constant within experimental error for the C_6^+ and C_8^+ ions, and are also independent of beam energy. It may be concluded that the saturated C_6^+ and C_8^+ carbonium ions react, after lifetimes of only a few μsec., from a common intermediate (or rapidly equilibrating intermediates) whether generated from the primary, secondary, or tertiary halides.[5] Presumably, primary, secondary, and tertiary cations interconvert with production, very predominantly, of the most stable tertiary cation, as expected from heats of formation data in the gas phase,[6] or n.m.r. data in solution.[7] Since cations formed by electron impact have characteristically different heats of formation,[6] skeletal reorganisation of the molecular ions prior to carbonium ion production can reasonably be exluded. It is noteworthy that molecular ions derived from isomeric hexanes and octanes do not isomerize to common structures even prior to decomposition *via* metastable transitions.[8]

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