Kinetic Isotope Effects in the Unimolecular Gas-phase Decomposition of Propane Radical Cations

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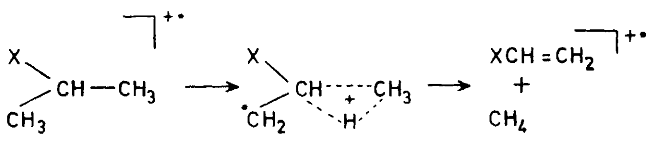
Summary A three-centre two-electron bond is involved in the transition state for loss of methane from the propane ion.

Extremely large isotope effects in the metastable peak intensities for loss of methane from the 2-methylpropane ion[1–3] have been interpreted[3] in terms of a secondary kinetic hydrogen isotope effect and an elimination mechanism involving three-centre two-electron bonding in the transition state (Scheme, X = Me). To determine whether similar isotope effects occur in the decomposition of the propane ion is important, first, because critical support could be provided for the mechanism proposed,[3] which constitutes a radically different view of alkane elimination reactions, and secondly, because although the propane ion has played a key role in establishing the quasiequilibrium theory (QET),[4–10] salient features of its chemistry have to date eluded satisfactory explanation within the framework of the theory. The proposed mechanism (Scheme, X = H) provides the needed explanation (*vide infra*).



Scheme

Metastable peak intensities (Table) for elimination of methane following electron impact of specifically deuterium-labelled propanes have been determined using an unusually large double-focusing mass spectrometer of reversed geometry.[11] The second field-free region (length 2700 mm), in which the decompositions of concern occur, represents a time-window from about 10 to 25 μs.

The loss of methane from metastable propane ions has been shown in earlier work to be a specific 1,2-elimination.[8] The results (Table) for $(CH_3CD_2CHD_2)^{+\cdot}$ show that there is both a large primary and a large secondary hydrogen isotope effect on the elimination of methane. The primary isotope effect is manifested in the relative intensities for loss of CH_4 and CH_3D, where an H atom and a D atom are competing in transferring to the CH_3 group. The secondary isotope effect can be seen in the relative intensities of CH_4 and CH_2D_2 loss, where an H atom is transferred in the one case to a CH_3 group and in the other to a CHD_2 group.

The large isotope effects are not evident in the results for $(CH_3CH_2CD_3)^{+\cdot}$ and $(CH_3CD_2CD_3)^{+\cdot}$ (Table) because the primary and secondary effects oppose and, it is suggested, largely cancel each other. The secondary effects are expected to be larger with these ions than with $(CH_3CD_2CHD_2)^{+\cdot}$ because they concern CD_3 rather than CD_2H groupings.

The secondary hydrogen isotope effect indicates that the C–H(C–D) bonds in the methyl group to be eliminated as methane are significantly *weaker* in the transition state than in the reactant ion. The reduction in vibrational frequencies leads to activation energies for eliminations of methane containing CH_3 being slightly lower than those for eliminations involving CHD_2.[3] The weakening of these C–H(C–D) bonds is accounted for by the mechanism in the Scheme (X = H). QET calculations by direct counting of states show that a 20% reduction in the C–H(C–D) stretches and bends of the $CH_3(CHD_2)$ and CD_2 groups reproduces the secondary isotope effects observed with $CH_3CD_2CHD_2$ (Table). The primary effect calls for larger reductions in the frequencies of the modes involving the transferred H(D).

The primary isotope effect is larger than the secondary with propane (Table), whereas the reverse is true with 2-methylpropane.[3] This difference can be explained in terms of the inductive or hyperconjugative effect of the methyl group stabilising the electron-deficient bond in the case of 2-methylpropane. The lower stability with propane means that the transferred hydrogen atom is bound less strongly to the two carbon atoms.

The persistent difficulty in treating the propane ion by QET has concerned the competition between loss of H· and loss of CH_4. The former has the lower appearance energy and appears to be a direct bond cleavage, whereas the latter must involve rearrangement. Yet as the internal energy rises (from about 70 to 120 kJ mol^{-1}), the rearrangement largely suppresses the direct bond cleavage.[4–10] Of a number of suggested explanations, the most plausible has been that the transition state for loss of H· is relatively tight, on the grounds that the product of the decomposition is cyclic.[7] However, the specificity of hydrogen loss (metastable ions eliminate only secondary hydrogen) and the fact that the isopropyl ion is the most stable of $(C_3H_7)^+$ structures,[12] weigh against the formation of a cyclic ion.

The mechanism advanced here naturally accommodates the ability of CH_4 loss to compete with H· loss, because the former has the looser transition state. The looseness arises from the weakening of the numerous C–H bonds involved

Table

Reactant ion	Relative intensities[a] for methane elimination			
	CH_4	CH_3D	CH_2D_2	CD_3H
$(CH_3CD_2CHD_2)^{+\cdot}$	0·87 ± 0·04	0·01 ± 0·03	0·12 ± 0·04	
$(CH_3CH_2CD_3)^{+\cdot}$		0·35 ± 0·05		0·65 ± 0·05
$(CH_3CD_2CD_3)^{+\cdot}$		0·29 ± 0·02		0·71 ± 0·02

[a] Intensities have been adjusted to allow for numbers of equivalent pathways, and also, in the case of $(CH_3CD_2CHD_2)^{+\cdot}$, to allow for the presence of $(CH_3CHDCD_3)^{+\cdot}$ (to the extent of 25%). Isotopic compositions have been determined by n.m.r. spectroscopy and field ionization mass spectrometry. Background pressure in field-free region was $<10^{-8}$ Torr.

with the electron-deficient 3-centre bond QET calculations show that the loss of CH_4 becomes more probable than loss of H· at about 25 kJ mol^{-1} above the activation energy of the former The activation energy for CH_4 loss[1,6,7,9,10] has been put at 97 kJ mol^{-1}, a C–C bending frequency has been taken as the reaction co-ordinate, 5 C–H stretches and bends have been reduced by 20% in the transition state, and the stretch and bend of the transferred H have been reduced by 50% The activation energy for H· loss[6,7,9,10] has been put at 91 kJ mol^{-1}, a C–H stretch has been taken as the reaction co-ordinate, and a C–H bending frequency has been reduced by 50% All other frequencies[13] have been kept the same in the reactant and the transition states of decompositions

Finally, by virtue of close analogy, the gas-phase mechanisms (Scheme), which rest upon the evidence of kinetic isotope effects, lend support to the C–C protiolysis mechanism put forward by Olah *et al* [14] for alkanes in superacid

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