Short Communications

On the Structural Integrity of Nascent Alkyl Radicals

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Isomerization by 1,2-hydrogen migration is a frequently observed phenomenon in carbonium ions, whereas 1,2-hydrogen migration in radicals has only rarely (if ever) been observed. Cation radicals behave in this respect like radicals and do not isomerize by 1,2-hydrogen shifts, while hydrogen rearrangements with larger transition states are well known within otherwise stable radicals and cation radicals. However, unimolecular fragmentation reactions of cation radicals are frequently accompanied by rearrangements that may involve 1,2-hydrogen migration. The fragmentation of gas-phase alkane cation radicals is a case in point. The reaction thermochromy for, e.g., formation of C4H9+ from the hexane or heptane molecular ions clearly shows that the C4H9+ ions cannot have retained the CH3CH2CH2CH2CH2 structure. Howe has presented direct experimental evidence for the occurrence of 1,2-hydrogen shifts in these reactions; in particular he has shown that C3H7 loss from the 2-methylhexane ion by cleavage of the C3–C4 bond takes place with simultaneous migration of the tertiary hydrogen:

\[
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3^+ \rightarrow \text{CH}_3\text{C}^+ + \text{C}_3\text{H}_7^-
\]

A number of similar reactions have been shown to occur in an analogous fashion, that is, with 1,2-hydrogen migration within the incipient ionic fragment. We recently suggested that for simple cleavage reactions isomerization by 1,2-hydrogen migration could occur also in the incipient radical. The experimental evidence presented in support of isomerization was the observation that the competing α-cleavage reactions of symmetrical (apart from deuterium labeling) amines such as I in the field-free regions of a mass spectrometer led to preferential loss of the unlabeled radical:

\[
\text{CH}_3\text{CHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CD}_3\text{H}_3 \rightarrow \text{[M–C}_4\text{H}_9]^+ \text{and} \text{[M–C}_4\text{H}_9\text{D}]^+
\]

The [M–57]/[M–58] ratio observed was 1.34. This was interpreted as a kinetic isotope effect on the elimination of the labeled radical, that is, as evidence for hydrogen rearrangement concurrent with C–C cleavage, leading to loss of tert-butyl radicals. A parallel study established that β-secondary deuterium isotope effects on closely related simple cleavage reactions were considerably smaller, typically around 1.10 per D.

However, a subsequent investigation demonstrated that intramolecular exchange of carbon and nitrogen bonded hydrogen atoms frequently occurs prior to fragmentation of primary and secondary amine cation radicals in the field free regions of a mass spectrometer. This, of course, invalidates the above observation as evidence for a 1,2-hydrogen shift in the incipient radical, since hydrogen/deuterium exchange as well as the operation of a kinetic isotope effect would lead to increased relative loss of unlabelled butyl radicals; indeed, CH/ND exchange in the N-labeled analog, 2, leads to loss of C4H9 as well as C4H9D– radicals by α-cleavage.

\[
\text{[CH}_3\text{CHCH}_2\text{NHCH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3]
\]

We have therefore investigated the competing α-cleavage reactions of the symmetrical tertiary amines 3 and 4, where the absence of NH groups precludes exchange reactions of this nature.
Rearrangement-cum-cleavage would in both cases lead to a more stable radical than would simple fission of the α C–C bond. Rearrangement in 3 would lead to loss of tert-butyl radicals, which are about 5 kcal/mol more stable than isobutyl radicals. For 4, 1,2-hydrogen migration concurrent with cleavage would lead to C₆H₅CH₂CH₂ rather than C₆H₅CH₂CH₂₂, where the difference in heats of formation is estimated to be ca. 13 kcal/mol, based on the bond dissociation energies (BDE) for primary alky C–H (Ref. 8) and secondary benzylic C–H (Ref. 9). A slightly higher value (17 kcal/mol) is obtained if the estimate is based on the stabilization energy for benzylic radicals together with the difference between the BDEs for primary and secondary aliphatic C–H. The [M–57]/[M–58] ratio observed for 3 is 1.10; the [M–105]/[M–107] ratio for 4 is 1.16 (1.08 per D). These ratios are very close to the values expected for β-secondary deuterium isotope effects, which establishes the absence of primary kinetic isotope effects on these reactions and in turn leads to the conclusion that the incipient radicals retain their structural identity during simple cleavage reactions.

Experimental. The isotope effects were determined as the ratio of the peak heights for the competing α-cleavage reactions in metastable ion spectra (MIKE spectra) recorded on double-focusing mass spectrometers of reversed geometry (magnetic analyzer preceding electric analyzer), using a wide collector slit. The α-cleavage ions carry more than 90 % of the fragmenting ion current for all compounds examined. The energy of the ionizing electrons was 70 eV. Measurements for 2 and 3 were performed on the unusually large double-focusing mass spectrometer (MMM) at the University of New South Wales (Sydney). The results for 4 were obtained on a VG ZAB–2F instrument at the University of Bielefeld.

Compound 2 was prepared from diisopentylamine by exchange with D₂O in the mass spectrometer inlet system. 3 was synthesized by reaction of the Grignard reagent derived from isobutylbromide-2-d with N-methoxymethyl-N-methylisopentylamine. Compound 4 was prepared by LiAlH₄ reduction of the N-(3-phenylpropyl)-N-methylamide of 3-phenylpropionic acid-3,3-d₂.

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