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CRACKING OF PROTONATED β,β-DIBRANCHED KETONES. THE IMPORTANCE OF STERIC EFFECTS IN THE β-SCISSION IN CARBONIUM IONS AND THE FATE OF t-BUTYL ION UNDER VARYING CONDITIONS

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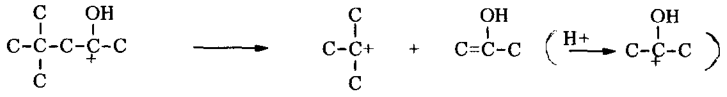
Protonated 3,3-dimethylpentanone-2 (I) cracks at elevated temperatures through β-scission into t-butyl ion and acetone:



$$C-\underset{C}{\overset{C}{C}}-C-\underset{+}{\overset{OH}{C}}-C \longrightarrow C-\underset{C}{\overset{C}{C}}{+} \;+\; C{=}\overset{OH}{C}-C \;\left(\xrightarrow{H+} C-\underset{+}{\overset{OH}{C}}-C\right) \qquad (1)$$

(I)

In FSO_3H-SbF_5 (molar ratio 5/1), this reaction has a rate constant of $4.4 \times 10^{-4} s^{-1}$ at 104° (E_A = 29.8 kcal.mole^{-1}, $\Delta S^{\neq} \sim 2$ e.u.). The rate is solvent-dependent, 10^4 k being 1.7 in FSO_3H and 0.53 in 98% H_2SO_4 at 104°, and 2.9 in 7% oleum, 2.8 in 98% H_2SO_4 and 1.9 in 92% H_2SO_4 at 115.5°. This solvent dependency, which bears no direct relation to the acidity of the medium, is supposed to be caused by cation-anion interaction, which increases according as the FSO_3^- or HSO_4^- concentration increases.

The cracking of (I) proceeds at a much lower rate than that of protonated 3,3,4,4-tetramethylpentanone-2 (II), which Dubois and Bauer (1) found to take place at a measurable rate in sulfuric acid at room temperature. We have confirmed this and have found that the cracking of II also proceeds much faster in FSO_3H-SbF_5 than in sulfuric acid. The higher rate of cracking of II as compared with that of I is probably caused by the mutual repulsion of the vicinal methyl groups, the release of which lowers the energy of activation of the fission reaction.

A considerable change in rate of cracking is observed in the case of cyclic ketones. There is no cracking of protonated 3,3-dimethylcyclohexanone at 155° in FSO_3H-SbF_5. 3,3-Dimethylcyclopentanone does not crack either; in FSO_3H-SbF_5 it is slowly converted (60% in 2.5 h) into 1,3-dimethylcyclopentenyl ion by rearrangements (H and CH_3 shifts) and dehydration.

The dramatic difference in stability towards cracking between the cyclic and acyclic hydroxycarbonium ions finds its cause in the stereochemistry of the β-scission reaction. For this reaction to proceed in a facile manner, the developing p_z orbital of the α-carbon atom must be parallel to the vacant p_z orbital of the C^+ carbon in the transition state (2). This arrangement is easily brought about in acyclic cations; in fact, it corresponds with the energetically preferred conformation about the C^+-C_α bond in these ions. In the cyclic ions, however, this is sterically impossible since it would require one of the α-hydrogen atoms to move towards the centre of the ring.

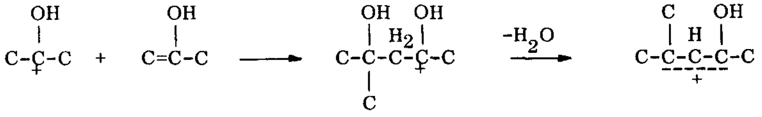
Of particular interest is the fate of the primary products of the cracking, which turned out to vary drastically with the conditions (solvent, temperature) under which they are formed.

Deno and coworkers (3) have shown that if t-butyl ions are generated, e.g. from isobutene or t-butanol, in concentrated sulfuric acid at room temperature, these ions react by polymerization, hydride-ion transfer and cyclization reactions to give eventually allylic polyalkylcyclopentenyl ions containing from 8 to over 18 carbon atoms as the stable ionic products. The t-butyl ions formed slowly by reaction (1) at a high temperature in sulfuric acid, however, yield as the major product a compound of which the PMR spectrum consists of two single lines at 6.04 and 4.37 ppm with an area ratio of 1 : 2. This compound, which is also formed in other reactions that generate t-butyl ions at a high temperature in sulfuric acid (e.g., the decarbonylation of trimethylacetic acid), has been identified as 2-methylenepropane-1,3-disulfonic acid (4). The reason why isobutene is sulfonated under these conditions and why it does not react to give polyalkylcyclopentenyl ions is the high efficiency of sulfuric acid in sulfonating isobutene, which causes a low steady-state concentration of t-butyl ion and isobutene as the result of which the rate of formation of polyalkylcyclopentenyl ions (which is second-order in t-butyl ion/isobutene (3)) is slowed down. The sulfonation reaction apparently has the higher activation energy, for the t-butyl ions generated in sulfuric acid at room temperature by the cracking of II are completely converted into polyalkylcyclopentenyl ions.

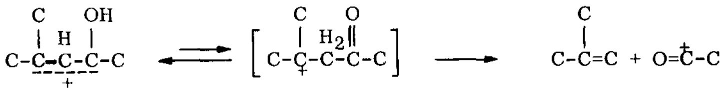
In FSO_3H or FSO_3H-SbF_5 (molar ratio 5/1), hardly any sulfonated products are formed, if it all, even at 100-130°, these acids being apparently much less effective sulfonating agents than sulfuric acid. In these acids, the t-butyl ion reacts to give 1,2,3-trimethylcyclopentenyl and at lower temperatures also some 1-methyl-3-ethylcyclopentenyl ions as the only alkylcyclopentenyl ions. The absence of higher molecular weight polyalkylcyclopentenyl ions is due to the circumstance that at a low steady-state concentration of isobutene/t-butyl ion the formation of the cyclopentenyl ring from C_8 carbonium ions predominates, kinetically or thermodynamically or both, over the trimerization and subsequent disproportionation reactions that eventually give rise to the formation of the whole scale of polyalkylcyclopentenyl ions.

This point is illustrated by the observation that if a concentrated (1M) solution of t-butyl ions in FSO_3H-SbF_5, which is stable at room temperature, is heated to 100° polyalkylcyclopentenyl ions are produced. It is evident that the technique of slow and controlled generation of t-butyl ions may find use in the elucidation of the reactions involved in the formation of polyalkylcyclopentenyl ions.

Nor is (protonated) acetone liberated in reaction (1) stable under all conditions. In sulfuric acid it reacts slowly to give protonated acetic acid and the sulfonation products of isobutene. This process involves dimerization of acetone to mesityl oxide (eq. 2) which subsequently cracks by β-scission to give isobutene and acetyl ion (eq. 3) (5). The occurence of these reactions has been verified by independent experiments.



(2)



(3)

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