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LETTERS TO THE EDITORS

Comments on "Denitrogenation of Piperidine on Alumina, Silica, and Silica-Aluminas: The Effect of Surface Acidity"

The recent paper by Miranda and co-workers (*1*) deals with the denitrogenation of piperidine over acid catalysts in relation to the mechanism of hydrodenitrogenation over sulfide catalysts. The results are discussed in terms of the heterolytic E2 β-elimination mechanism: the nitrogen in the piperidine ring is quaternized by protonation on a Brønsted acid site and β-hydrogen is abstracted by a basic site, resulting in C–N bond cleavage. The mechanism is in good agreement with the data obtained and is consistent with the previous knowledge on deamination and other similar reactions such as dehydration, dehydrosulfurization, and dehydrohalogenation over solid acid catalysts. However, this mechanism is designated in the above-mentioned paper (*1*) as a "classical Hofmann elimination mechanism." The purpose of this letter is to show that such nomenclature is incorrect and misleading.

Splitting of the C–N bond by heterolytic E2 β-elimination is promoted by quaternization of the nitrogen atom and by attack of the base on β-hydrogen. In normal organic chemistry (in the absence of a solid catalyst), the quaternization of nitrogen by protonation does not lead to β-elimination. The base does not attack the β-hydrogen, but the most acidic hydrogen in the molecule, which is the hydrogen bonded to nitrogen. The deprotonization of an amine occurs instead of β-elimination.

The crucial idea of the Hofmann elimination is the prevention of the attack of the base on the hydrogen bonded to the nitrogen atom by removal of all of these hydrogens. They are removed by exhaustive methylation of the nitrogen atom (e.g., (*2*)). β-Hydrogens become the most acidic hydrogens in the molecule, and the elimination is achieved by the thermal decomposition of the tetraalkyl ammonium salt. The presence of any hydrogen bonded to nitrogen is incompatible with the Hofmann elimination method.

Quaternization of the nitrogen atom in amines can be achieved in various ways. The term "Hofmann elimination" is solely related to the quaternization made by exhaustive methylation. For instance, the β-elimination of amine oxides, where the nitrogen atom is quaternized by oxidation, is not called Hofmann elimination (e.g., (*2*)).

In the β-elimination of amines catalyzed by solid acid–base catalysts, the base does not attack the hydrogen bonded to the nitrogen atom because of geometrical reasons. Acid and base species are localized on separate sites of the surface. The base attacks the second most acidic hydrogen in the molecule, and that is the β-hydrogen.

Deamination of amines over alumina and other acid catalysts has been studied in a number of previous papers. In addition to the papers mentioned in the work of Miranda and co-workers (*1*), Ref. (*3*) also gives an additional useful survey of the literature. Up to 1979, no paper seems to mention the term "Hofmann elimination" in connection with deamination over solid catalysts. This misleading reference to Hofmann elimination was probably given for the first time in Nelson and Levy's paper (*4*) on the possible role of β-elimination in the mechanism of hydrodenitrogenation. This has been repeated in several other papers (e.g., (*1, 5–7*)).

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The mechanism of hydrodenitrogenation over sulfides seems to be the topical theme in hydrorefining catalysis, and the present comments might be useful in clarifying the terminology. In summary, the terms "β-elimination" and "Hofmann elimination" are not identical. Hofmann elimination is one very special type of β-elimination. Its characteristic feature is that the nitrogen atom is quarternized by exhaustive methylation. The mechanism of deamination discussed in Ref. (*1*) is heterolytic E2 β-elimination (or simply β-elimination), similar to the mechanism of some dehydrations, dehydrosulfurizations, dehydrochlorinations, etc. However, reference to this mechanism as a Hofmann reaction is misleading because quaternization of the nitrogen atom by exhaustive methylation is not involved.

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