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NOTES

The Organic Chemistry of Hydrodenitrogenation

The importance of hydrotreatment processes for the removal of heteroatoms from fossil fuel liquids is increasing, owing to both economic and environmental constraints. In response to the recent increases in the price of crude, interest in the upgrading of heavy residual fractions and the use of petroleum alternatives such as shale oil or coal liquids has refocused attention on both hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) processes.

Historically, more attention has been given to HDS. However, in the last few years HDN is being recognized as an important part of heavy fuel processing. It is the more difficult and more demanding of the two hydrotreating reactions, and requires more severe reaction conditions than does HDS (*1*, *2*). Like sulfur, bound nitrogen is generally contained as a heteroatom in a five- or six-membered aromatic ring; structures related to pyrrole, indole, carbazole, pyridine, quinoline, isoquinoline, and acridine are the most common (*3*). Most of the studies of the HDN reaction use one of these N-heterocycles as a model compound and employ a supported Mo or W oxide with or without CoO or NiO promoters as a catalyst.

In the most recent investigations of the reaction, it has been found that denitrogenation requires a much larger hydrogen consumption than desulfurization, owing to the obligatory complete saturation of carbon atoms either bound directly to nitrogen or one carbon atom removed from it. This high hydrogen requirement was noted for HDN both in the absence (*4–9*) or presence (*2*, *7*, *10–13*) of sulfur. In contrast, ring hydrogenation is not required for HDS (*2*). Furthermore, the presence of sulfur, either as H_2S or an organic sulfur compound, results in an increase in the rate of removal of bound nitrogen (*1*, *2*, *10–12*) and promotes the rate of reduction of the nitrogen-containing aromatic ring (*1*, *12*). The effect is observed when sulfur is in excess of the amount required for sulfidation of the catalyst.

For the most part, the above-referenced studies comprise kinetic analyses of HDN for various model compounds. Very few of these reports attempt to rationalize the data in terms of a detailed reaction mechanism. However, the kinetic data presented by these authors can be used to support a generalized mechanism for HDN chemistry. This will be outlined in this note.

A detailed mechanism for the chemistry of the HDN process must be consistent with the following observations:

Complete saturation of α and β carbon bound to nitrogen is required before nitrogen removal is possible.

H_2S, or its precursors, enhances the rate of nitrogen removal.

H_2S enhances the rate of reduction of nitrogen-containing heterocyclic aromatic rings.

Intermediate structures such as *N*-pentylpiperidine appear during HDN of pyridine.

The rupture of the carbon–nitrogen bond is not a facile process; the amine functionality is known to be a very poor leaving group for either displacement or elimina-

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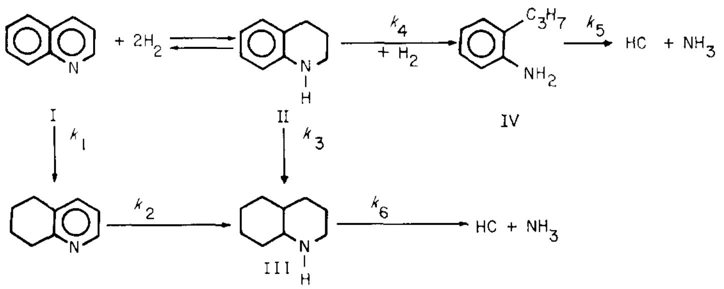
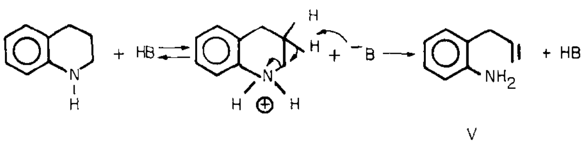
tion reactions (*14*). In fact, the most common amine removal reaction, the Hofmann degradation (*15*), usually requires that the leaving nitrogen be quaternized before the reaction becomes feasible. The removal is known to occur only with saturated hydrocarbons. A corresponding process for the reductive elimination of nitrogen from an *unsaturated* carbon is not known. *Thus, the high hydrogen requirement of HDN is consistent with the known reductive degradation chemistry of carbon–nitrogen bonds.* This similarity therefore suggests that nitrogen is removed from heavy feedstocks and coal liquids via reactions similar to the classical Hofmann degradation.

In illustrating this proposed mechanism, quinoline will be used as the model compound. However, identical mechanisms can be written for the other nitrogen heterocycles found in heavy feeds. With quinoline (I) the HDN process has been found to follow the paths given in the following scheme (*11, 12*).

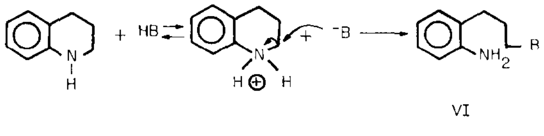


It should be noted that carbon–nitrogen bond scission *only* occurs from the saturated carbon species, II and III. Furthermore, both k_4 and k_6 are found to increase in the presence of H_2S (*12*).

Ring opening of II to yield 2-propylaniline (IV) can occur via an elimination or displacement reaction. Both of these reactions are catalyzed by a base. The ring opening elimination reaction is shown in reaction (1), while the displacement process is illustrated in reaction (2).



(1)



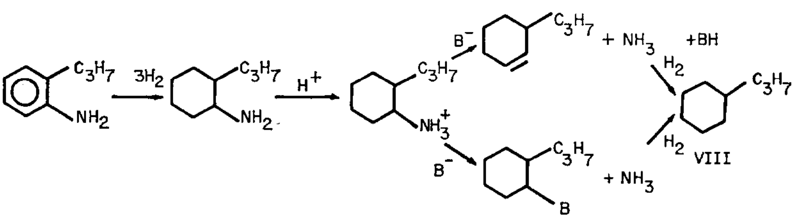
(2)

In both of these cases, the initial ring-opened product (either V or VI) would be rapidly converted to the observed intermediate, IV, under the prevailing reaction conditions via hydrogenation of the double bond (V) or hydrogenolysis of the sulfhydryl group (VI). A similar displacement process can account for the appearance of *N*-pentylpiperidine (VII) during HDN of pyridine in the absence of H_2S (*8*).

Again, initial saturation of the heterocyclic ring is required. The base required in the elimination step can be supplied by a surface oxide, an amine, or H_2S via the following dissociation:

$$H_2S \Leftrightarrow H^+ + {}^-HS \qquad (3)$$

Removal of the $-NH_2$ group from 2-propylaniline (IV) is required to complete the HDN of quinoline via step 5 in the scheme. This step again requires saturation of an aromatic ring; the overall process is shown below:



(4)

The simplest nitrogen-free product would be *n*-propylcyclohexane (VIII) obtained at the expense of 7 moles of H_2 for removal of one nitrogen atom. Similar steps can be written for the other reaction paths from quinoline.

In summary, the above-described Hofmann degradation chemistry is consistent with the experimental observations reported for HDN reactions in the absence and presence of sulfur. It explains the observed high hydrogen requirement and elucidates the role played by H_2S in the nitrogen-removal steps. Several important implications can be drawn from this analysis. The chemical requirement of carbon saturation prior to nitrogen removal suggests that *the high hydrogen consumption of HDN is unavoidable for nitrogen removal under reductive conditions.* However, the rate of denitrogenation can be improved by increasing the acidity of the catalyst, in particular when reactions are conducted in the absence of sulfur. In the presence of sulfur, the nitrogen removal reaction is enhanced by the displacement reaction as well as by facilitating the Hofmann degradation. Sulfur addition may therefore be indicated in the treatment of feedstocks with low sulfur and high nitrogen contents.

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