

STERIC EFFECTS IN THE HYDROGENATION-HYDRODENITROGENATION
OF ISOMERIC BENZOQUINOLINES CATALYZED BY SULFIDED
Ni-W/Al₂O₃

J. Shabtai*, L. Veluswamy, and A.G. Oblad

Department of Mining and Fuels Engineering,
University of Utah, Salt Lake City, Utah 84112

Mechanistic aspects of sulfide-catalyzed hydrodenitrogenation of N-heterocyclics, and in particular of condensed polycyclic systems, have been studied to a limited extent (1,2). Recently, this subject has attracted more interest and several significant kinetic studies have been reported (3,4). It is noteworthy, however, that so far very little attention has been paid to stereochemical aspects of hydrodenitrogenation processes. In order to obtain a first information on the possible importance of steric effects in such reactions, the hydrogenation-hydrodenitrogenation of two isomeric benzoquinolines, i.e. 5,6-benzoquinoline (1) and 7,8-benzoquinoline (2), was comparatively studied as a function of reaction temperature, hydrogen pressure, and sulfided catalyst type. Experiments were carried out in a semi-batch reactor, and products formed were identified and analyzed by a combination of gas chromatography, PMR, and mass spectrometry.

RESULTS AND DISCUSSION

Figures 1-4 summarize the change in product composition from hydrogenation of the two isomeric benzoquinolines as a function of reaction temperature in the range of 200-380°C, using a sulfided Ni-W/Al₂O₃ catalyst. As seen from Fig. 1, at temperatures below 250°C, the only product from 2 is 1,2,3,4-tetrahydro-7,8-benzoquinoline (3), derived by selective hydrogenation of the pyridine ring. With increase in temperature above 250°C, there is fast decrease in the yield of this intermediate compound, accompanied by formation of three other derivatives, i.e., 6-propyl-1,2,3,4-tetrahydronaphthalene(4), 2-propylnaphthalene(5), and 1,2,3,4,11,12,13,14-octahydro-7,8-benzoquinoline(6). The presence of compounds 5 and 6 indicates that hydrodenitrogenation of the primary product 3 could occur with or without preliminary hydrogenation of the end benzene ring. It is noted that the yield of 2-propylnaphthalene (5) reaches a maximum at ca 300°C and then decreases with increase in temperature, while the yield of 6-propyl-1,2,3,4-tetrahydronaphthalene(4) continues to increase up to 350°C and only then decreases with further increase in temperature (Fig. 1). This would indicate that 5 plays an important role as a precursor in the formation of 4. The latter could also be derived from 6, but the relatively low yield of this compound indicates that this alternative pathway is of lesser importance. At temperatures between 350-380° (Figure 2) the decrease in the concentration of 4 is accompanied by a corresponding increase in the yield of 2-propyldecalin(7), which is the final product of the hydrodenitrogenation process. At the relatively short contact time of 2 hr, at 341°C, the yield of 2-propyldecalin(7) is only 9%, and 6-propyl-1,2,3,4-tetrahydronaphthalene(4) is the major product (79%). However, at a contact time of 7 hr hydrogenation of 4 into 7 is essentially complete.

Patterns closely similar to those in Figs. 1 and 2 are found in the change of product composition as a function of hydrogen pressure.

Figures 3 and 4 summarize the change in product composition from hydrogenation of 5,6-benzoquinoline(1) as a function of reaction temperature. As seen, at temperatures around 200°C the single product observed is 1,2,3,4-tetrahydro-5,6-benzoquinoline (8), derived by fast, selective hydrogenation of the pyridine ring in 1. The indicated rate of this reaction is higher by at least one order of magnitude than that of the corresponding hydrogenation of 7,8-benzoquinoline(2) to 1,2,3,4-tetrahydro-7,8-benzoquinoline(3). At temperatures > 200°C there is gradual decrease in the

*Weizmann Institute of Science, Rehovot, Israel

concentration of 8, accompanied by formation of 1,2,3,4,11,12,13,14-octahydro-5,6-benzoquinoline(9). The yield of this second-step hydrogenation intermediate reaches a maximum around 300°C, and then decreases at higher temperature (Fig. 3). Further, this decrease in the yield of 9 (Fig. 4) is accompanied by a corresponding gradual increase in the yield of the hydrodenitrogenation product, 5-propyl-1,2,3,4-tetrahydronaphthalene(10), indicating that hydrodenitrogenation is mainly accomplished subsequent to the saturation of the end benzene ring. As seen from Fig. 4, at temperatures >300°C the product contains also small amounts (5-8%) of 1-propylnaphthalene (11), indicating that direct hydrodenitrogenation of the primary product 8 occurs to a minor extent. At reaction temperatures of ca 340-380° part of compound 10 is further hydrogenated to give 1-propyldecalin (12) which can be considered as the final product of the hydrodenitrogenation process. If the temperature is kept at ca 340°C and the reaction time is extended, or the pressure increased, compound 10 is converted largely into 12, without any significant extent of cracking. At ca 380°C, however, some cracking of compound 10 occurs to form 1,2,3,4-tetrahydrohaphthalene (Fig. 4).

The study of the reaction of 5,6-benzoquinoline(1) as a function of catalyst type indicates that there is no significant difference in the hydrogenation-hydrodenitrogenation activity of sulfided Ni-W/Al₂O₃ and Ni-Mo/Al₂O₃ catalysts.

The observed markedly slower hydrogenation of the pyridine ring in 7,8-benzoquinoline(1) can be ascribed to the steric hindrance effect of the 7,8-benzo group, which prevents edgewise adsorption of the pyridine ring to acidic sites on the catalyst surface by means of the nitrogen electron pair(5). In contrast, hindrance-free adsorption of this type, with consequent strong polarization and activation of the pyridine moiety is easily attained in the case of 5,6-benzoquinoline(1). Following the hydrogenation of the pyridine rings in 1 and 2 to give 1,2,3,4-tetrahydro-5,6-benzoquinoline(8) and 1,2,3,4-tetrahydro-7,8-benzoquinoline(3), respectively, there are marked differences in the subsequent reaction pathways leading to hydrodenitrogenation of these two isomeric intermediates, i.e. compound 3 undergoes direct hydrodenitrogenation to yield 2-propylnaphthalene(5), whereas 8 undergoes essentially complete hydrogenation of the end benzene ring, to form 1,2,3,4,11,12,13,14-octahydro-5,6-benzoquinoline(9), prior to the hydrogenolysis step (*vide supra*). This could be ascribed to differences in the steric characteristics of the intermediates involved. Examination of molecular models shows that in compound 3 the N-atom is in a *peri*-position relative to the aromatic H at C-14. This should cause some displacement of the nitrogen out of coplanarity with the aromatic system, and should facilitate the hydrogenolysis of the C-N bonds, leading to formation of 2-propylnaphthalene(5). In contrast, the 5,6-benzo group in 8 does not interact sterically with the hydrogenated pyridine ring, *viz.* in this case there is no destabilizing effect upon the C-N bonds. Consequently, 8 is hydrogenated to compound 9 prior to the hydrogenolysis step, which produces 5-propyl-1,2,3,4-tetrahydronaphthalene(10).

The results obtained indicate that the rate and depth of hydrodenitrogenation of coal-derived liquids may strongly depend on the steric characteristics of condensed N-heterocyclic-aromatic components, or of partially hydrogenated reaction intermediates formed during the process.

EXPERIMENTAL

The apparatus, as well as the experimental and analytical procedures were essentially the same as used in the preceding study of phenanthrene and pyrene hydrogenation.

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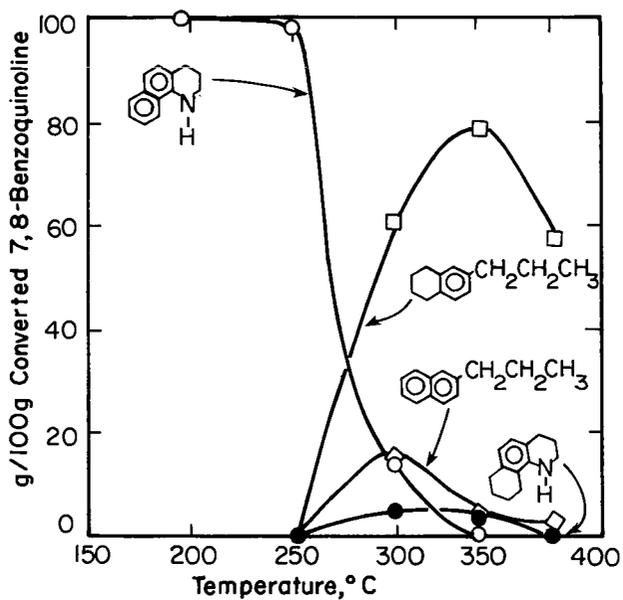


Fig. 1. Change in product composition from hydrodenitrogenation of 7,8-Benzoquinoline as a function of temperature (Stage A).

Catalyst: Sulfided Ni-W/Al₂O₃
 Pressure: 2900 psig;
 Reaction time: 2 hr.

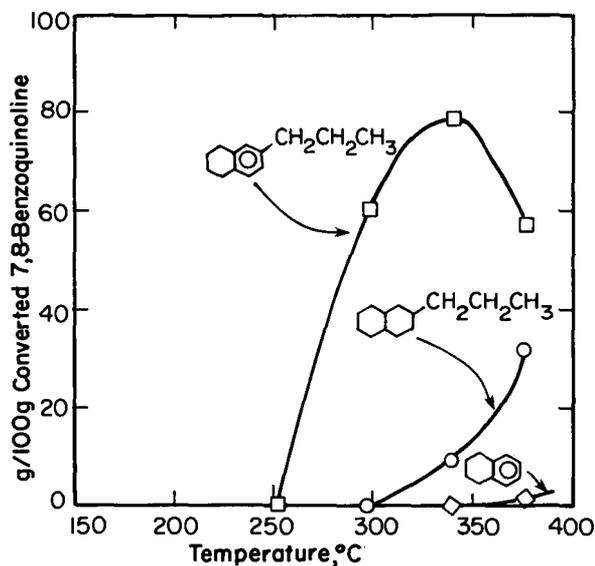


Fig. 2. Change in product composition from hydrodenitrogenation of 7,8-Benzoquinoline as a function of temperature (Stage B).

Catalyst: Sulfided Ni-W/Al₂O₃
 Pressure: 2900 psig;
 Reaction time: 2 hr.

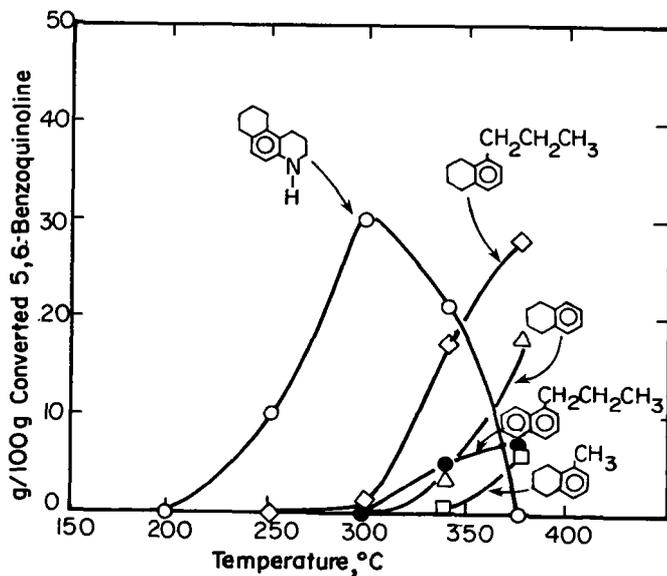


Fig. 4. Change in product composition from hydrodenitrogenation of 5,6-Benzoquinoline as a function of temperature (Stage B).

Catalyst: Sulfided Ni-W/Al₂O₃
 Pressure: 2900 psig;
 Reaction Time: 2 hrs.

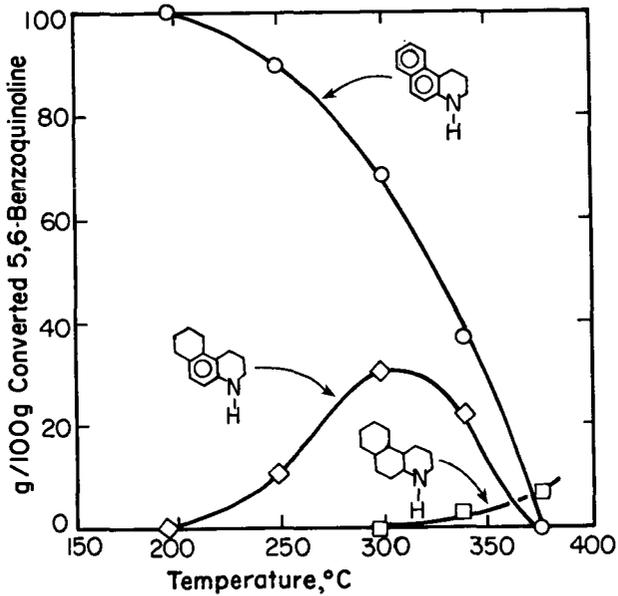


Fig. 3. Change in product composition from hydrodenitrogenation of 5,6-Benzoquinoline as a function of temperature (Stage A).

Catalyst: Sulfided Ni-W/Al₂O₃
 Pressure: 2900 psig;
 Reaction Time: 2 hrs.