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**CONTROL OF CATALYTIC HYDROTREATING SELECTIVITY
WITH AMMONIA**

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SUMMARY

We have discovered that the presence of a low concentration of ammonia greatly reduces the rate of hydrogenation of an aromatic compound (propylbenzene) on an industrial NiMo/Al₂O₃ catalyst while under similar conditions it has only a mild inhibiting effect on hydrodenitrogenation (of quinoline). This suggests a method under industrial reaction conditions of minimizing undesired aromatic hydrogenation during catalytic hydrodenitrogenation and thus significantly reducing hydrogen consumption. We plan to explore this effect in more detail by model compound studies.

We originally proposed to use initially a mixture of naphthalene and quinoline since we have an extensive background on the HDN kinetics of quinoline. However coal liquids contain substantial amounts of a base fraction that consists of hydroxy pyridines, hydroxy indoles and/or hydroxy anilines. No information has been published on the HDN-HDO hydrotreating reactions of a compound in which a hydroxyl (phenolic) group is attached to a heterocyclic N compound. Thus the question has been raised of the extent to which quinoline HDN may or may not reflect the behaviour of such compounds. We have therefore performed a limited study with 8-hydroxy quinoline dissolved in tetralin utilizing a NiMo/Al₂O₃ catalyst in a packed bed reactor operating at 360°C and 385°C and 6.9 MPa.

We find that the N-heterocyclic ring is hydrogenated first to form an equilibrium mixture with a reaction intermediate that has been identified as 8-OH-1,2,3,4-tetrahydroquinoline. Oxygen is then removed to form the same reaction intermediates we have observed from quinoline alone, but in somewhat different ratios.

The important conclusion, by extension, is that with hydroxy-N-heterocyclic

compounds in general the OH group will likely be removed rapidly at the beginning of reaction and that the subsequent reaction network will be similar to that previously established for the parent N-heterocyclic compound as such.

EXPERIMENTAL

The reactor consisted of a vertical 0.52-cm-i.d. tube immersed in a fluidized sand bath to maintain isothermal conditions. Liquid was fed through a preheater coil to the top of the catalyst bed by a high-pressure liquid chromatography pump (Milton Roy Constametric III). Similarly, hydrogen was fed through a preheater coil by a mass flow controller (Brooks). The liquid and hydrogen feeds were mixed at the reactor inlet, passed downward through the catalyst bed, and flashed through a back-pressure regulator (Grove). This equipment have been used in our laboratory in previous studies of HDN, HDO, and HDS and is described in more detail elsewhere (Satterfield and Yang, 1984).

Reactants. The feed consisted of a solution with a concentration of 0.245 mol/L of 8-hydroxyquinoline (99+ % pure, Aldrich) in tetralin (99% pure, Aldrich). This corresponds to ~3.7 wt% of 8-hydroxyquinoline in solution or 0.35 wt% N and 0.4 wt% O. H_2S was produced in situ by the decomposition of 1-dodecanethiol (98% pure, Aldrich) which was added to the feed. Under reaction conditions, 0.12 mol/L of 1-dodecanethiol reacts rapidly to generate 12 kPa of H_2S . The operating conditions were 360°C and 385°C and 6.9 MPa total pressure. Hydrogen (Airco grade 4.5 and Med-Tech prepurified, >99.99% purity, were used interchangeably) was fed at a rate of 1520 mL at STP/mL of liquid, equivalent to 9000 SCF H_2 /barrel (SCF = Standard Cubic Feet at 60°F), to produce an initial 8-hydroxyquinoline pressure of 24 kPa. Note that our

definition of space time is based on per mole of 8HQ fed, not total moles of liquid fed. Hence, a space time of 320 (h g of catalyst)/mol of 8HQ corresponds to a liquid hourly space velocity (LHSV) of 9.4 h^{-1} for the 8HQ concentration used here.

Catalyst. The catalyst used was a commercial NiMo/Al₂O₃ (American Cyanamid HDS-3A). The catalyst was crushed and sieved to a size range of 150-212 μm . After drying in air at 110°C overnight, a full charge of catalyst (1.6 g) was diluted 4:1 with a similar sized inert SiC and packed into the reactor tube. After the reactor was purged under helium flow for 12 h at 100°C, the catalyst was presulfided with a 10% mol H₂S in H₂ gas mixture. The gas flow rate was 40 mL/min at a total pressure of 0.24 MPa. Sulfiding temperature was maintained at 175°C for 6 h, and the temperature was then raised to 315°C at a rate of 1°C/min. The gas flow was switched to helium after sulfiding had continued for 1 h at 315°C.

For the first 200 h after sulfiding, HDN of 4 wt% quinoline in a C₁₆ paraffin mixture was performed for routine deactivation of the catalyst until there was a steady level of activity. The routine deactivation was conducted at 360°C and 6.9 MPa total pressure. Standard catalyst activity was measured at a space time of 320 (h g of catalyst)/mol of quinoline under the same conditions.

Analysis. Liquid samples of the reactor effluent were collected downstream from a low-pressure phase separator, and analyzed on a Perkin-Elmer Sigma 1B gas chromatograph equipped with dual flame ionization detectors. Concentrations of the products were related to the starting liquid feed. Carbon mass balances on total products compared to 8-hydroxyquinoline disappearance ranged from 90 to 105%. Separation of reaction species was accomplished by using either Supelco SPB-35 (30

meters, 0.25mm ID, 0.25 μ m) or Supelcowax 10 (30 meters, 0.25mm ID, 0.25 μ m) columns. Compounds were identified by comparing their retention times to those of pure standards. An unknown intermediate was identified by electron impact (EI) and NO₃/chemical ionization mass spectrometry, performed for us under the direction of Dr. T.C. Ho at Exxon Research and Engineering.

RESULTS

Figure 1 shows a simplified reaction mechanism of the HDN of quinoline adapted from Satterfield and Smith (1986). Quinoline (Q) undergoes rapid hydrogenation equilibrium to form 1,2,3,4-tetrahydroquinoline (PyTHQ) which either reacts to form 2-propylaniline (OPA) or decahydroquinoline (DHQ). Both OPA and DHQ undergo C-N hydrogenolysis to form the clean denitrogenated products. In addition, quinoline is hydrogenated to 5,6,7,8-tetrahydroquinoline (BzTHQ) which can be further hydrogenated to DHQ.

The hydrotreatment of 8HQ produced the same reaction intermediates found during the HDN of Q, but the amount of BzTHQ formed was much greater at low space times (Fig. 7). Further, a new intermediate was observed, but only at low space times. Figure 2 shows a plot of the ratio of the concentration of this intermediate to that of 8HQ at two temperatures. Since the ratio is independent of space time, we surmised that the intermediate is in equilibrium with 8HQ. Because the equilibrium is established rapidly we inferred that this is a hydrogenation equilibrium. Thus, either the heterocyclic pyridine ring or the aromatic benzene ring in 8HQ is being hydrogenated to form an 8-hydroxytetrahydroquinoline.

Effect of Higher Temperature on the Intermediate. Figure 2 shows the

equilibrium ratio between 8HTHQ and 8HQ at 385°C. The equilibrium constant decreases with increased temperature. The heat of reaction calculated from Figure 2 for the hydrogenation of 8HQ to intermediate is 27.5 kcal/mol, a value comparable to that reported by Satterfield et al. (1978) for the thermodynamic equilibrium between Q and PyTHQ. Thus, equilibrium between 8HQ and the intermediate is further justified.

Determination of the structure of the intermediate. The analysis of the intermediate was performed using electron-impact ionization (EI) and ND₃/chemical ionization (CI) mass spectrometric techniques. Figure 3 shows the EI mass spectrum which indicates that the molecular weight of the intermediate is 149, the molecular weight of the two 8-hydroxytetrahydroquinolines. However, because no reference spectrum is available, the exact structure of the intermediate cannot be determined.

An ND₃/CI mass spectrometric technique was used to determine the number of exchangeable hydrogens in the molecule. If there are no exchangeable hydrogens, the deuterated molecular ion in the ND₃/CI spectrum should be two mass units higher than the molecular weight. Figure 4 shows that the deuterated molecular ion of the unknown is four mass units above the molecular weight. There are two exchangeable hydrogens on the molecule, corresponding to the -OH and =NH groups. Thus, the unknown intermediate is 8-hydroxy-1,2,3,4-tetrahydroquinoline (8HTHQ).

Reaction Network. Figure 5 shows the possible reaction network of the 8HTHQ. Abstraction of the -OH group would convert it to PyTHQ from which the reaction network of quinoline via PyTHQ would proceed. However, during the course of HDO of phenolic compounds two paths have been observed, direct abstraction of the oxygen, or hydrogenation followed by C-O hydrogenolysis. Li et al (1985) studied the HDO of

1-naphthol and find it to proceed through two pathways. Odebunmi and Ollis (1983) studied the HDO of cresols and also find the dual path behavior. Figure 6 shows this behavior as applied to 8HTHQ. The benzene ring in 8HTHQ can be hydrogenated to 8-hydroxydecahydroquinoline (8HDHQ) followed by rapid C-O hydrogenolysis to form DHQ or direct C-O hydrogenolysis to form PyTHQ.

The above mechanism explains some of the reaction paths of the 8HTHQ, but cannot account for the high concentration of BzTHQ observed. Figure 7 shows a comparison of the concentrations of BzTHQ in the reactions of 8HQ and Q at 360°C. A higher concentration of BzTHQ is generated from the hydrotreatment of 8HQ than from the HDN of Q. If all of the 8HQ had reacted via 8HTHQ to PyTHQ then the same concentration of BzTHQ should be observed as in feeding pure Q since PyTHQ and Q are in thermodynamic equilibrium under reaction conditions (Satterfield et al., 1978). The presence of a higher concentration of BzTHQ during the hydrotreatment of 8HQ indicates that not all of the 8HQ is reacting to PyTHQ, further corroborating the existence of a path from 8HQ to DHQ. However, the increased concentration of DHQ is not enough to justify the high concentration of BzTHQ observed because the reaction of BzTHQ to DHQ is heavily favored towards DHQ (Satterfield and Smith, 1986). Therefore, 8HQ must also be reacting to BzTHQ through a third route, i.e., 8HQ is hydrogenated to 8-hydroxy-5,6,7,8-tetrahydroquinoline (8HTHQa) which undergoes HDO very rapidly to form BzTHQ. Figure 8 shows the completed proposed mechanism. Compounds in brackets are not observed directly in the liquid samples, but are speculated to exist during reaction.

DISCUSSION

Based on the results of previous studies of simultaneous HDN and HDO of separate molecules (Satterfield and Yang, 1983; LaVopa and Satterfield, 1988), HDN precedes HDO because of the more favorable adsorption of nitrogen compounds. However, the reaction mechanism shown in Figure 8 establishes that HDO goes to completion before HDN for 8HQ. The presence of the intermediate, 8HTHQ, indicates attachment of 8HQ to the catalyst surface by the pyridine ring. 8HQ being locked in place by the adsorption of the pyridine ring may allow for the removal of the oxygen. The ease of removal of the -OH group may thus be a function of its location on the ring. This may depend on the orientation of the hydroxyquinoline relative to the catalyst surface. For example, the oxygen in 5-hydroxyquinoline may not come off as easily if hydroxyquinolines are attached perpendicular to the surface at the lone pair of electrons of the nitrogen. More likely, the hydroxyquinolines are attached flatly onto the surface, facilitating hydrogenation of the rings.

Selectivity. The reaction species observed during the reaction of 8HQ include 8HTHQ and those species observed during the HDN of Q. The final selectivity to clean hydrocarbons remains unaffected by the presence of the -OH group. The clean products include propylcyclohexane (PCH), propylcyclohexene (PCHe), and propylbenzene (PB) with PCH predominating. The ratio of PB to PCH was unchanged between the HDN of Q and the hydro treatment of 8HQ. There was slightly more variability in the PCHe to PCH ratio.

List of Acronyms

BzTHQ	5,6,7,8-tetrahydroquinoline
CI	chemical ionization
DHQ	decahydroquinoline
EI	electron ionization
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
OPA	2-propylaniline
PB	propylbenzene
PCH	propylcyclohexane
PCH _e	propylcyclohexene
PyTHQ	1,2,3,4-tetrahydroquinoline
Q	quinoline
8HQ	8-hydroquinoline
8HDHQ	8-hydrodecahydroquinoline
8HTHQ	8-hydroxy-1,2,3,4-tetrahydroquinoline
8HTHQ _a	8-hydroxy-5,6,7,8-tetrahydroquinoline

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Figure 1: Simplified reaction mechanism of HDN of quinoline adapted from Satterfield and Smith, 1986.

Figure 2: Ratio of intermediate (8HTHQ) to 8HQ versus space time. 8HTHQ in equilibrium with 8HQ at low space times.

Figure 3: The molecular ion in the EI spectrum indicates that the molecular weight of the unknown is 149.

Figure 4: Two exchangeable hydrogens were found in the molecule of the unknown compound by comparing the mass of the deuterated molecular ion with the molecular weight.

Figure 5: Abstraction of $-OH$ from 8-hydroxy-1,2,3,4-tetrahydroquinoline (BHTHQ) to enter HDN of quinoline network.

Figure 6: Dual path HDO of 8-hydroxy-1,2,3,4-tetrahydroquinoline (8HTHQ) to enter HDN of quinoline network.

Figure 7: Comparison of BzTHQ formation. More BzTHQ is formed during hydrotreatment of 8HQ than during HDN of Q.

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