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Simultaneous Hydrodenitrogenation and Hydrodeoxygenation of Model Compounds in a Trickle Bed Reactor

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In selected binary mixtures of a heterocyclic nitrogen compound and a phenolic or heterocyclic oxygen compound and in the presence of H_2S, the rate of hydrodeoxygenation (HDO) was considerably decreased in comparison to that observed with the same compound individually at the same reaction conditions. In mixtures, the rate of hydrodenitrogenation (HDN) of quinoline was increased and the effect on the HDN rate of *o*-ethylaniline depended on the specific oxygen compound. Small concentrations of water vapor increase hydrodenitrogenation, especially if H_2S is also present. In the hydrodeoxygenation of an ethyl phenol, substantial quantities of an ethyl cyclohexene are formed as an intermediate. The final products are ethylcyclohexane and ethylbenzene, the former predominating.

INTRODUCTION

Synthetic liquid fuels derived from coal, oil shale, and tar sands contain significant amounts of sulfur and nitrogen compounds. Those from coal also contain substantial amounts of oxygen-containing species. The sulfur and nitrogen content is lowered by hydrotreating, usually in a fixed bed or a trickle bed reactor at a hydrogen pressure in the range of about 7 to 14 MPa and temperature in the range of 300 to 400°C. Usually a catalyst of CoMo, NiMo or NiW supported on alumina is employed and is presulfided *in situ*. It is not clear whether combined oxygen removal is necessarily required during this hydrotreating to achieve desired product specifications. In any event, if oxygen-containing species are present, they may react, and because of the high oxygen content of coal liquids this can cause significant additional hydrogen consumption.

An extensive literature exists on hydrodesulfurization (HDS), a lesser amount on hydrodenitrogenation (HDN), but relatively little attention has been paid to how oxygen species may affect HDS or HDN or the nature of the reaction networks of hydrodeoxygenation. Furimsky (*1, 2*) studied the hydrodeoxygenation of a heavy hydrocracked gas oil from hydrocracking of Athabasca bitumen, Qader *et al.* (*3*) of a low temperature coal tar, Sullivan *et al.* (*4*) of shale oils. Badilla-Ohlbaum *et al.* (*5, 6*) and Rollmann (*7*) studied the simultaneous HDS, HDN, and HDO reactions occurring in a mixture of several model compounds. In both cases, dibenzofuran was used to represent the oxygen compound in the model feedstock. Rollmann further determined the reactivity of several other phenol and furan derivatives by substituting them one at a time for dibenzofuran in the model mixture. Recently Krishnamurthy *et al.* (*8*) did a detailed kinetic study on the HDO of dibenzofuran. Weisser and Landa (*9*) reviewed the earlier literature on hydrogenation of alcohols, ketones, aldehydes, and phenols over sulfide catalysts.

Upon reacting the heteroatoms in hydroprocessing, hydrogen sulfide, ammonia, or water is ultimately formed. Elsewhere we have reported on the enhancing effect of H_2S on hydrodenitrogenation of model compounds on a NiMo catalyst (*10–12*).

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The effect of water vapor on sulfide catalysts is not yet clear. Lipsch and Schuit (*13*) reported a poisoning effect of water on the oxide form of cobalt molybdena catalyst. We found that 13.3 kPa of water in 6.9 MPa of H_2 exerted little influence on quinoline HDN in the vapor phase over a sulfided nickel molybdena catalyst, but with no hydrogen sulfide added to the feed (*14*). In a brief study with a sulfided $CoMo/Al_2O_3$ catalyst at 300°C and 7.3 MPa and in the presence of 200 kPa of H_2S, Goudriaan (*15*) reported that the concentration of water vapor had no effect on the conversion of pyridine but enhanced the hydrogenolysis of the intermediate piperidine, for an overall increase in HDN, but the effect occurred chiefly at water partial pressures above 100 kPa.

Phenol derivatives predominate among the oxygen compounds in liquid fuels derived from coal, oil shale, and tar sands. For example, Ignasiak *et al.* (*16*) reported that 75% of the oxygen present in an Athabasca asphaltene was in the form of hydroxyl functions. In a detailed analysis of an anthracene oil, Scheppele *et al.* (*17*) reported that 81% of the acids were hydroxylated aromatics. Furans are also found. For the present study, *m*-ethylphenol, *o*-ethylphenol, benzofuran, benzylether, and benzodioxan were chosen as model compounds.

Quinoline (Q) is a good model compound for the six-membered ring heterocyclic nitrogen compounds in the middle distillate range of fuels. We have developed the reaction network for its HDN reactions by a series of studies in the vapor phase (*18–20, 11*), and in the liquid phase in a trickle bed reactor (*21*). Shih *et al.* (*22*) have also studied quinoline HDN in the liquid phase. We have also made considerable study of *o*-ethylaniline (OEA) and other alkylanilines by themselves since the HDN of anilines is a significant rate-limiting step in the overall HDN reactions. With this background we used quinoline and OEA as standard reference nitrogen compounds in this study.

EXPERIMENTAL

The reactions were carried out in a trickle bed reactor, described in detail elsewhere (*21*). All data reported here were obtained at a gas-to-liquid ratio of 1600 cm^3 of H_2 at STP per cm^3 of liquid carrier (equivalent to 9000 standard cubic feet of hydrogen per barrel of oil), a pressure of 6.9 MPa, and a temperature of 375°C, over a presulfided $NiMo/Al_2O_3$ catalyst (American Cyanamid HDS 3A), which was also used in our previous vapor phase and liquid phase work. Products formed were determined from liquid samples analyzed by gas chromatography (Perkin–Elmer Sigma 1B), using a capillary column SE-54 (Hewlett–Packard). Peaks were identified by previous GC/MS studies and by peak spiking. Detailed analysis procedures are given in the thesis of Yang (*23*).

All experiments were performed with a solution in an inert paraffin carrier liquid, consisting mainly of *n*-hexadecane, of either a nitrogen compound alone, an oxygen compound alone, or a binary mixture of a nitrogen compound and an oxygen compound. In every case the concentration of each heterocyclic compound was 3.87×10^{-4} mole/g liquid feed (hydrocarbon + additive) and, except where specified, 0.74 wt% of CS_2 was also added. This is rapidly converted to H_2S in the reactor. In a binary mixture the N plus O compound concentration was 7.74×10^{-4} mole/g of liquid feed. All studies were at 6.9 MPa and 375°C and product compositions were determined over a range of contact times. As in previous papers, space time is defined here in terms of moles of heterocyclic compound, not in terms of total liquid. The nitrogen concentration of each of the two *N*-heterocyclic compounds corresponds to 0.54 wt% N and that of the oxygen compounds to 0.62 wt% O.

Most of the studies were done with one catalyst charge, termed charge #5, consisting of 1.6 gm of catalyst diluted 1 : 4 with inert. It was presulfided by procedures de-

scribed elsewhere for catalyst charges 2 and 3 (*21*). One set of runs with quinoline and various concentrations of *m*-ethylphenol in the presence or absence of H_2S (results shown in Figs. 9 and 11) was performed with a different catalyst charge, termed charge #6, identical to #5 and presulfided by the same procedure except that the sulfiding time was twice as long. Consequently this charge was slightly more active. All the experiments above were done with CS_2 in the feed, except for one specific limited study described later.

With both charges, all data reported here were obtained after the catalyst had reached steady state activity, and catalysts were periodically resulfided as described elsewhere (*21*).

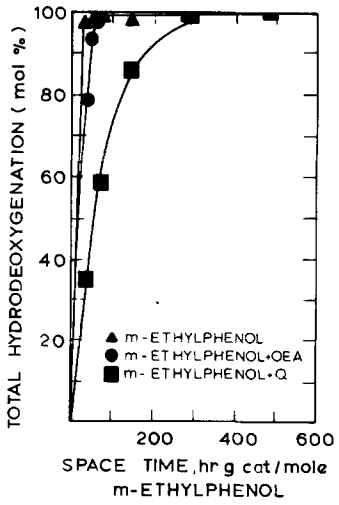


FIG. 1. Hydrodeoxygenation of *m*-ethylphenol alone or in presence of *o*-ethylaniline (OEA) or quinoline (Q).

RESULTS

Results can be discussed in terms of the effects of a heterocyclic nitrogen compound on hydrodeoxygenation (HDO) and the effects of an oxygenated compound, or water formed from it, on hydrodenitrogenation (HDN). The values of percent HDO presented here are based on unreacted oxygen compound in the product liquid compared to the amount in the feed.

Material balances on oxygen reactant in and reactant plus products out sometimes showed a moderate loss. This may be due to the boiling points of these oxygen compounds, which at atmospheric pressure are 219°C for *m*-ethylphenol, 205°C for *o*-ethylphenol, and 174°C for benzofuran, compared to quinoline, 238°C. Some reactant could be lost in the vapor phase but the major loss is probably of the hydrocarbon products. For example, atmospheric boiling points for ethylcyclohexane and ethylbenzene are 132 and 136°C, respectively. This, however, would not affect the reported percent conversions. Frequently several minor peaks appeared in the GC analysis of the product that were not identified. They comprised up to about 1% of the total.

Effect of a Nitrogen Compound on Hydrodeoxygenation (HDO)

In all cases the presence of a nitrogen compound substantially decreased the rate of HDO and quinoline (Q) caused a greater degree of inhibition than *o*-ethylaniline (OEA).

m-Ethylphenol. The HDO reaction of this compound when studied alone went to completion even at the shortest space time used. As shown in Fig. 1, quinoline reduces the HDO rate substantially but OEA reduces the HDO reaction rate to a lesser degree. Either with or without the presence of a nitrogen compound, the products resulting from the HDO of *m*-ethylphenol are two isomers of ethylcyclohexene, ethylbenzene, ethylcyclohexane, and methylethyl cyclopentane. Trace amounts of diethylcyclohexane (several isomers) were also identified.

Figure 2 shows the distribution of major products observed as a function of contact time, in the presence of quinoline. Two isomers of ethylcyclohexene were formed in substantial concentration as intermediates. The dominant final hydrocarbon product was ethylcyclohexane, with methylethylcyclopentane comprising about 10% of the to-

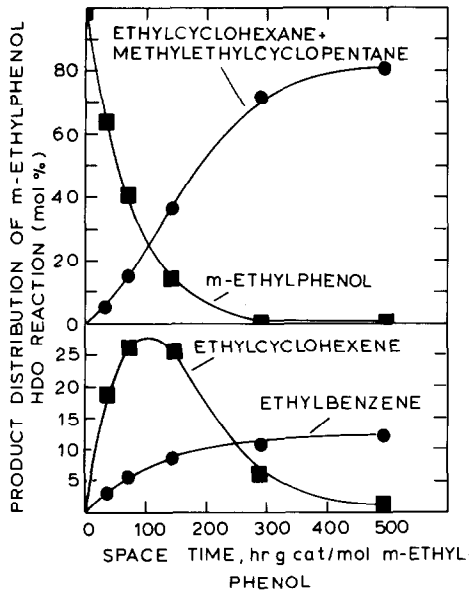


FIG. 2. Distribution of hydrocarbon products from HDO of *m*-ethylphenol. Quinoline present.

tal. These two isomers could not be separated completely at room temperature or higher by gas chromatographic analysis, but they were identified by the use of GC/MS (*23*).

o-Ethylphenol. The HDO of *o*-ethylphenol by itself was also so fast that reaction was completed at the shortest space time studied (Fig. 3). The products formed here are similar to those in the HDO reaction of *m*-ethylphenol, but about 10% of the final hydrocarbon product was diethylcyclohexane (several isomers) and about 3.5% was diethylbenzene (several isomers). The presence of quinoline not only slows the HDO reaction, but also significantly hinders the side reactions for forming diethylcyclohexane and diethylbenzene. Comparison of Figs. 3 and 1 shows that the ortho isomer is less reactive than the meta isomer. Similarly, Rollmann (*7*) reported that sterically hindered phenols (*o*-ethyl and 2-phenyl) were considerably less reactive than nonsterically hindered phenols (*p*-cresol and 4-propylphenol).

Figure 4 shows that the change in distribution of major products with contact time is similar to that from the *m*-ethyl isomer except that the maximum in the ethylcyclohexene concentration is lower and occurs at a longer contact time. This is consistent with *o*-ethylphenol being less reactive.

Benzofuran. Benzofuran is less reactive than the ethyl phenols (Fig. 5). The first significant intermediate product isolated is

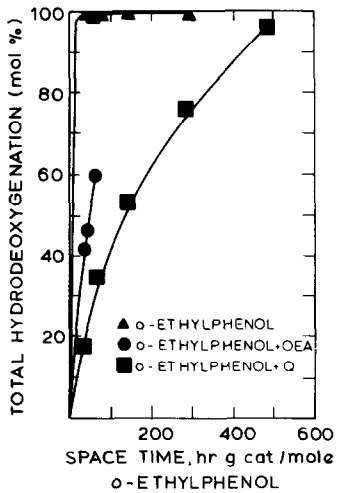


FIG. 3. Hydrodeoxygenation of *o*-ethylphenol alone or in presence of *o*-ethylaniline (OEA) or quinoline (Q).

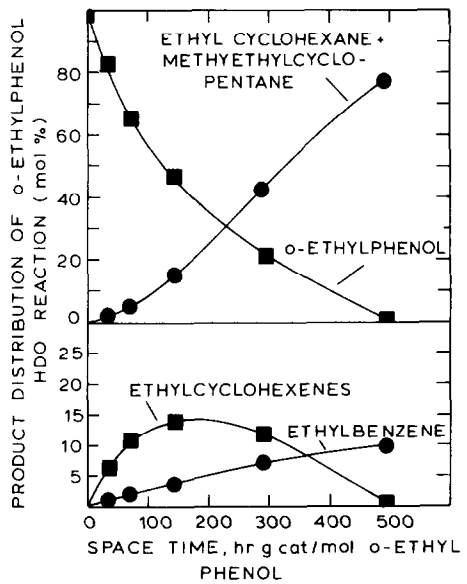


FIG. 4. Distribution of hydrocarbon products from HDO of *o*-ethylphenol. Quinoline present.

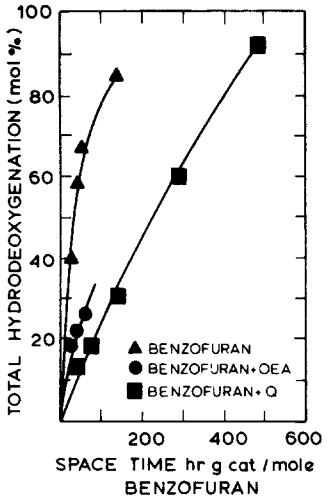


FIG. 5. Hydrodeoxygenation of benzofuran alone or in presence of *o*-ethylaniline (OEA) or quinoline (Q).

o-ethylphenol, which then undergoes the set of reactions described above (Fig. 6). A trace of dihydrobenzofuran was also found.

Benzylether. With benzylether alone the catalyst bed became plugged. With quinoline also present, the reactor did not plug but the benzylether disappeared completely even at the shortest space time studied, 36 hr g-cat/mole benzylether. A mass balance indicated that some side reactions occurred. The dominant identified product was methylcyclohexane, comprising 50 to 85 mole% of the benzylether reacted. Toluene was formed in amounts equivalent to less than 1 mole% of the reactant. Benzylether will crack thermally (*24*) and in the absence of hydrogen, growth and polymerization reactions will readily occur. It is not clear whether the plugging here was the result of formation of polymers or of paraffin-insoluble substances.

Benzodioxane. The catalyst bed quickly became plugged, either in the presence or absence of quinoline.

DISCUSSION OF HYDRODEOXYGENATION REACTIONS

The inhibiting effect of nitrogen compounds can be attributed to competitive adsorption, which has been observed in several reactions over hydrotreating catalysts, for example, competitive adsorption among intermediates within the quinoline HDN reaction network (*19*), between quinoline and indole (*25*), and between thiophene and pyridine (*10*). Quinoline has a greater inhibiting effect than OEA in a plug flow reactor because the latter undergoes the HDN reaction considerably faster (compare Figs. 7 and 10).

At least some of the catalytic sites are acidic in nature, and therefore within a mixture the accessibility of a compound to these sites is related to its basicity. In general, quinoline and its HDN reaction intermediates 1,2,3,4-tetrahydroquinoline (PyTHQ), 5,6,7,8-tetrahydroquinoline (BzTHQ), decahydroquinoline (DHQ), *o*-propylaniline (OPA), and ammonia are strong or moderate bases, while the oxygen species and their presumed reaction intermediates are very weak bases or neutral molecules. Thus the various nitrogen compounds can greatly reduce the adsorption of oxygen compounds, and thus inhibit the HDO reactions.

Particularly noteworthy here is the observation that ethylcyclohexene is formed

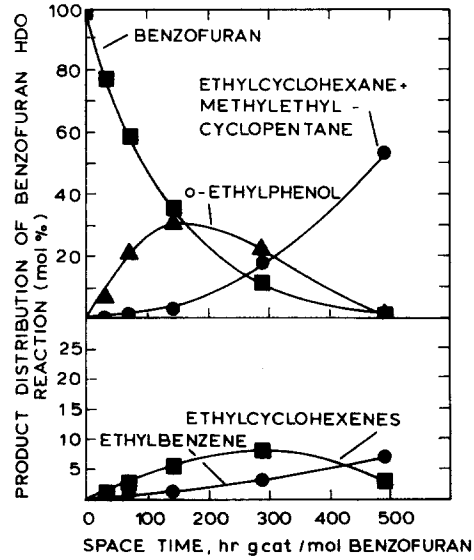


FIG. 6. Distribution of hydrocarbon products from HDO of benzofuran.

from ethylphenols in major quantities as a reaction intermediate. This suggests that the phenol is first hydrogenated, followed by fast removal of the hydroxyl group to form water and an ethylcyclohexene.

The HDN reaction network of *o*-ethylaniline and of *o*-propylaniline, analogous compounds to the ethylphenols, has been studied in detail including identification of products by GC/MS analysis (*21*). An analogous series of reactions occurs there. The aromatic ring of *o*-propylaniline is first hydrogenated and then a subsequent fast reaction forms NH_3 and propylcyclohexene. The latter in turn either dehydrogenates to form propylbenzene (PB), becomes hydrogenated to propylcyclohexane (PCH), or isomerizes and becomes hydrogenated to methylpropylcyclopentane. With a NiMo/Al_2O_3 catalyst, in either the HDO of an ethyl phenol or the HDN of an alkylaniline, the principal hydrocarbon product ultimately formed is an alkylcyclohexane rather than an alkylbenzene. Benzofuran appears to be first hydrogenated to dihydrobenzofuran which is then converted rapidly to *o*-ethylphenol.

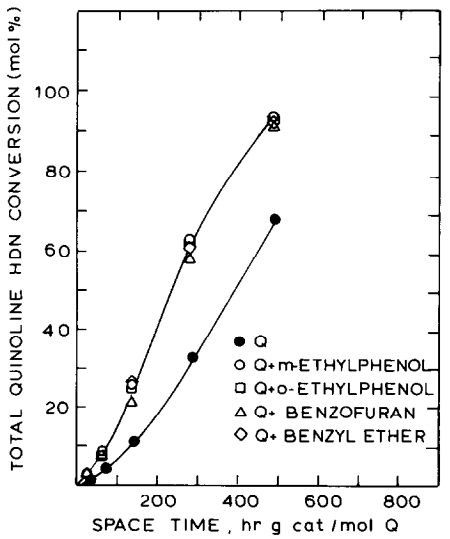


FIG. 7. Oxygen compounds enhance HDN of quinoline (Q).

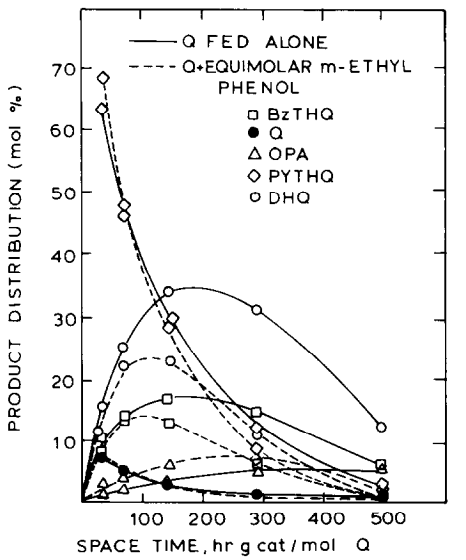


FIG. 8. *m*-Ethylphenol alters the relative distribution of intermediate products in HDN of quinoline (Q). PyTHQ = 1, 2, 3, 4 tetrahydroquinoline; BzTHQ = 5, 6, 7, 8 tetrahydroquinoline; DHQ = decahydroquinoline; OPA = *o*-propylaniline.

DISCUSSION OF HYDRODENITROGENATION REACTIONS

Enhancement of Quinoline HDN by Oxygen Compounds

Although quinoline reduces the rate of HDO reactions, all four oxygen compounds studied significantly enhanced the rate of quinoline HDN, as shown in Fig. 7. The distribution of intermediate products is also significantly altered, as shown in Fig. 8 for the case when *m*-ethylphenol was added to quinoline. Notably the maximum amount of decahydroquinoline (DHQ) in the product distribution decreases significantly, and is shifted towards a shorter space time. DHQ is formed by hydrogenation reactions from BzTHQ and PyTHQ and then undergoes a hydrogenolysis reaction which is a rate-limiting step in the HDN reaction network. The early hydrogenation reactions are much more rapid, which leads to the conclusion that hydrogenolysis activity is significantly enhanced by the presence of an oxygen compound.

As in the absence of oxygen compounds, the principal hydrocarbon products are propylcyclohexene, formed as an intermediate, plus propylbenzene, methylpropylcyclopentane, and propylcyclohexane, the last predominating.

The presence of *o*-ethylphenol, benzofuran, or benzylether each has an effect similar to *m*-ethylphenol on the product distribution of quinoline HDN (data not shown). This observation plus the fact that the oxygen compounds react rapidly suggests that the acceleration of quinoline HDN by oxygen compounds is caused by the water resulting from the simultaneous HDO reaction.

m-Ethylphenol or Water Accelerates Quinoline HDN in Presence of H_2S

In studying how water directly affects quinoline HDN, in our present apparatus we could not add water separately so we were limited by the very low solubility of water in the liquid carrier. This amounts to approximately 0.01 wt% at room temperature. Therefore, 4.7, 0.95, or 0.19 wt% of *m*-ethylphenol in quinoline were compared with a quinoline solution saturated with water. At our typical reaction condition, 6.9 MPa and 375°C, and at a fixed space time of 494 hr g-cat/mole Q, the feed was switched back and forth from quinoline alone to a feed containing quinoline plus a specified amount of *m*-ethylphenol or saturated with water.

The quinoline HDN conversion was determined for each feed composition after reaching steady state (Fig. 9). Reproducibly, the quinoline HDN conversion increases if *m*-ethylphenol or water is present and decreases when an oxygen species is absent. The slight decrease in catalyst activity with time is caused by the continuous operation without intermediate resulfiding of the catalyst. After 80 hours of operation on stream, resulfiding restored catalyst activity to its original steady state value, corresponding to 73% quinoline HDN conversion as shown by the starred point on Fig. 9.

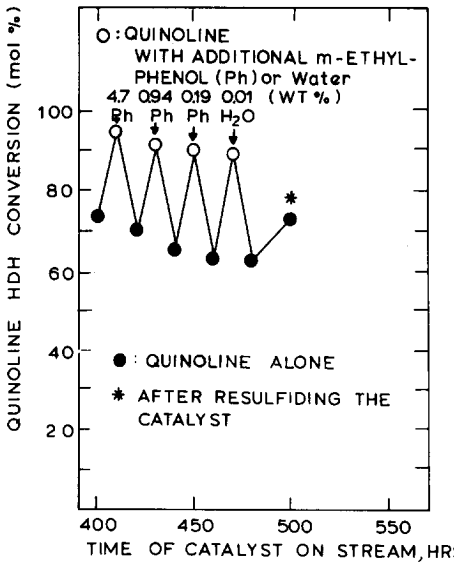


FIG. 9. Addition of *m*-ethylphenol (Ph) or water increases the HDN of quinoline. H_2S present.

Notably the same degree of increase in HDN conversion occurs independent of *m*-ethylphenol concentration and is produced by even a trace of water. This is additional evidence that the enhancing effect of the oxygen compound originates from the water formed by its reaction.

Effect of Oxygen Compounds on HDN of o-Ethylaniline (OEA) in Presence of H_2S

The presence of *m*-ethylphenol or *o*-ethylphenol increases the HDN of *o*-ethylaniline, but benzofuran decreases it slightly, as shown in Fig. 10. Benzofuran is the most stable of the three oxygen species and less of it reacted than the OEA.

The addition of 0.01 wt% of water to *o*-ethylaniline at a space time of 55 hr g-cat/mole OEA had no effect on its HDN, which remained constant at 50%, in contrast to the effect on quinoline. Since the HDN reaction of OEA is kinetically controlled by the hydrogenation of its aromatic ring, this suggests that hydrogenation activity is not significantly changed by a trace amount of

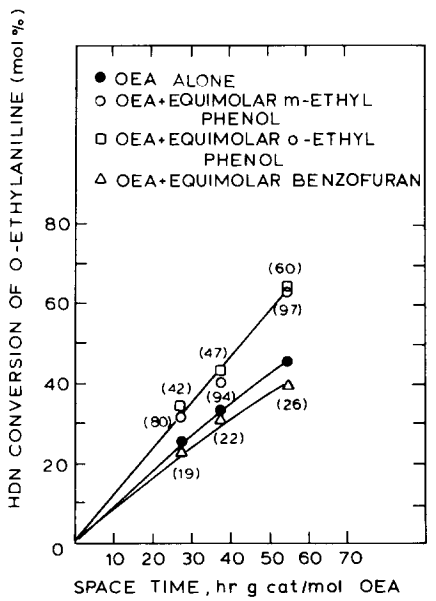


FIG. 10. Phenols increase the HDN of *o*-ethylaniline (OEA) but benzofuran decreases it. Numbers in parentheses are the % HDO of the oxygenated compound.

water. Comparing the effects on quinoline and OEA indicates that a trace of water vapor significantly increases hydrogenolysis activity but has little effect on hydrogenation activity.

Proposed Mechanisms

The presence of an oxygen compound can change hydrogenation activity either by affecting hydrogenation sites on the catalyst surface, or possibly by forming a hydrogen bond complex between the hydroxyl group and the nitrogen atom of OEA. The first mechanism most likely involves the interaction of the catalyst surface with water rather than with the oxygen compound directly, and such structural change would presumably be affected by the concentration of water resulting from the HDO reaction. This can explain why 4.7 wt% of *m*-ethylphenol exerts an increase on *o*-ethylaniline HDN but 0.01 wt% of water does not. The low HDO conversion observed with benzofuran suggests that competitive adsorption between OEA and benzofuran plays a more prominent role than the influence of water vapor. The fact that *m*-ethylphenol and *o*-ethylphenol have the same effect on HDN even though their degree of reaction is different suggests that the alteration of catalyst structure may be completed above some minimum partial pressure of water. (However, see alternate explanation below.)

Hydrogen bonding between the hydroxyl group of an oxygen species and the nitrogen atom of OEA occurs readily (*16, 26*). This may inhibit, to some degree, the adsorption of OEA onto catalyst sites through its nitrogen atom, and thus increase the probability of adsorption of the aromatic ring of OEA. This would cause faster hydrogenation and faster HDN of *o*-ethylaniline. There are several parallel ideas in the literature. When pyridine is reduced catalytically in the form of a salt or in acid solution, hydrogenation proceeds more rapidly than when it is reacted as a base in a neutral solvent (*27*). This is caused by shielding of the nitrogen atom by the acid or the formation of a salt. Substitution in positions two and six has a favorable effect on pyridine hydrogenation (*28*), which suggests that physical shielding by a group or groups adjacent to the nitrogen atom plays a role in the ring hydrogenation of pyridine.

The hydroxyl group on either a phenol or water can facilitate hydrogen bonding, so the fact that *m*-ethylphenol and *o*-ethylphenol have the same effect on HDN even though their HDO conversions differ significantly can be interpreted within this framework.

The effect of oxygen compounds on HDN of OEA is therefore attributed to two opposite influences, an increase from hydrogen bonding or a decrease by competitive adsorption. In general, the adsorption of oxygen compounds and their HDO reaction intermediates is expected to be weaker than those of nitrogen compounds and of HDN reaction intermediates, but it depends on the specific nature of the species present. Benzofuran does not have a hydroxyl group to form a hydrogen bond, and

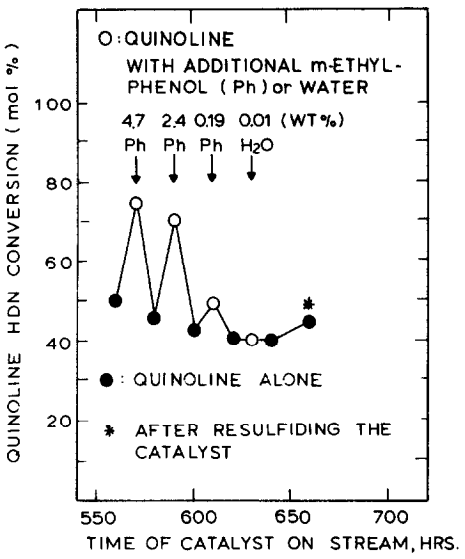


FIG. 11. Enhancement of quinoline HDN by *m*-ethylphenol (Ph) or water is less in absence of H_2S.

its HDO conversion is relatively low, so the water produced may not provide enough hydrogen bonding to enhance the hydrogenation of OEA and competitive adsorption is the more dominating effect.

In the HDN of quinoline, OPA is formed at a later stage in the reaction (Fig. 8) and is present in much smaller concentration than when OEA was studied directly in the same initial concentration as that of quinoline. By the time OPA is formed in the quinoline HDN network, there are enough hydroxyl groups, either from water or oxygen molecules present, to form hydrogen bonds and thus result in an increase in OPA hydrogenation.

Interactions of Hydrogen Sulfide and of Water on Quinoline HDN

In the studies discussed above, the enhancement of hydrogenolysis activity by the presence of water was observed with feeds containing 0.74 wt% CS_2. It is remarkable that only 0.01 wt% of water (about 0.4 kPa partial pressure) can exert such a marked effect.

If CS_2 is omitted from the quinoline, however, somewhat higher partial pressures of water are required to show this enhancement. Figure 11 shows the results of repeating the runs in Fig. 9 but in the absence of H_2S. *m*-Ethylphenol present in 4.7 or 2.4 wt% concentration causes a similar degree of increase in quinoline HDN as in the presence of H_2S, but 0.19 wt% of this compound exerts a much smaller increase, while 0.01 wt% of water has no effect at all. If all the phenol were converted to water, the corresponding partial pressures for these three concentrations would be 29, 14.5, and 1.2 kPa, respectively. This presents interesting questions about how water interacts with hydrogenolysis sites and how hydrogen sulfide may be incorporated into this process.

We observed almost no effect of 13.3 kPa partial pressure of water on quinoline HDN at 6.9 MPa total pressure in a vapor phase study (*14*), using the same catalyst presulfided but with no added hydrogen sulfide during reaction. In the present study, in the absence of added CS_2, an increase in quinoline HDN was noted with as little as 0.19 wt% of *m*-ethylphenol. Even assuming complete HDO, this amounts to a considerably smaller concentration of water (1.2 kPa) than was used in the vapor phase study. It is not clear whether this is an intrinsic difference between liquid phase and vapor phase processing or whether there is a different effect if water is produced directly from a HDO reaction, in which it may be more effectively adsorbed onto the catalyst surface.

Hydrogen sulfide, if present in the reactor, can cause a structural change in the sulfided molybdena catalyst. Water may be incorporated in such process, resulting in more Brønsted acid sites on the catalyst surface, and thus increased hydrogenolysis activity. Without the structural alteration of the catalyst provided by the presence of hydrogen sulfide, the interaction of water with a sulfided molybdena catalyst may require a much higher concentration of water. The interaction of water with the alumina alone

does not seem to be a likely effect, for this should be independent of hydrogen sulfide.

Relative Reactivities of Oxygen and Nitrogen Heterocyclic Compounds

Several generalizations have been published concerning the relative rates of HDS, HDN, and HDO on various catalysts and concerning the relative rates of destruction of various specific S, N, and O compounds by hydrotreating. Such comparisons can be misleading unless carefully qualified since reactivity is dependent on several factors.

(1) The presence of water, ammonia, and/or hydrogen sulfide can affect the rate of reaction significantly.

(2) Activity is related to the basic molecular structure of the reactant, e.g., six-membered heterocyclic N ring compounds (pyridines) versus five-membered ring compounds (pyrolles); phenol versus furan type of oxygen compounds.

(3) In mixtures, competitive adsorption effects can dominate. The accessibility of a molecule to the catalyst surface is affected by its basicity.

(4) Steric hindrance plays a role.

(5) Within a homologous series, activity decreases with increasing molecular weight.

(6) Most reactions are not simple first order, so a relative ranking can vary with initial concentration or with percent conversion studied.

Keeping the above in mind, some specific comparisons can be made from the present studies.

o-Ethylphenol and o-ethylaniline. *o*-Ethylphenol by itself undergoes the HDO reaction much faster than *o*-ethylaniline undergoes HDN by itself, as shown in Fig. 12. In a mixture, HDN increases moderately and HDO drops greatly and the two reactions become comparable.

Benzofuran and quinoline. The HDO reaction of benzofuran is much faster than the HDN reaction of quinoline if each compound is studied separately. In a mixture, the conversion of quinoline is increased and that of benzofuran is decreased, as shown in Fig. 13, and the conversions become similar even though benzofuran and quinoline have different basicities and different molecular structures.

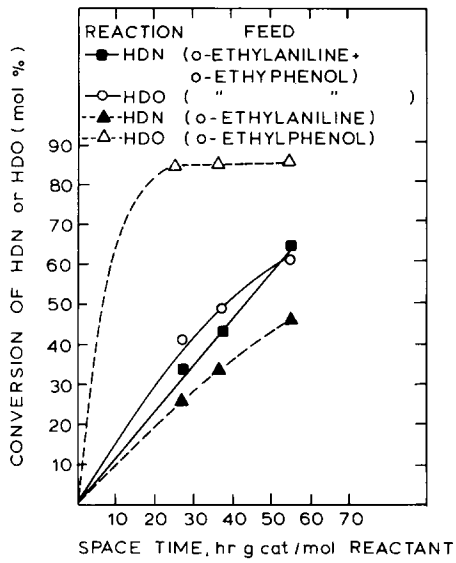


FIG. 12. In a mixture, the HDO of *o*-ethylphenol is decreased markedly and the HDN of *o*-ethylaniline is increased moderately. H_2S present.

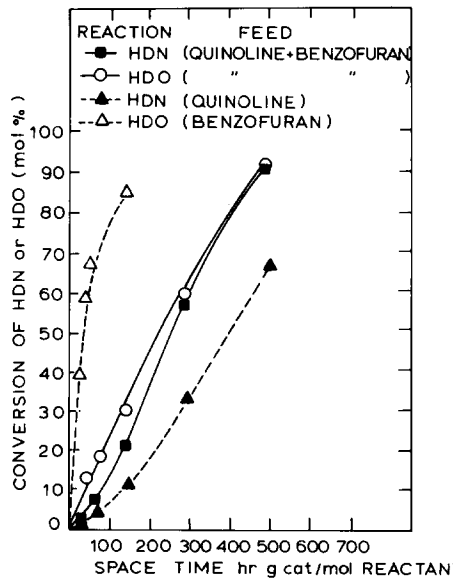
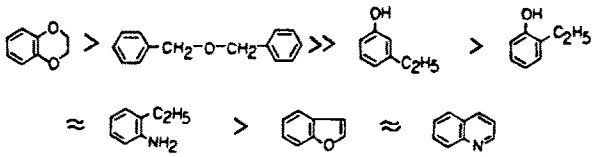


FIG. 13. In a mixture, the HDO of benzofuran is decreased and the HDN of quinoline is increased.

Oxygen species. As individual compounds, the HDO reactions of both ethylphenols were complete even at the shortest space time studied, and that of benzylether alone led to catalyst bed plugging. In Fig. 14 we compare each of their reactivities, as well as that of benzofuran in the presence of an equimolar quantity of quinoline, which slows all HDO reactions. Benzylether is more reactive than the two ethylphenols, which in turn are more reactive than benzofuran. *m*-Ethylphenol is more active than *o*-ethylphenol, presumably due to steric hindrance of the ethyl group at the ortho position.

Order of reactivities. The reactivities of the five oxygen compounds and two nitrogen compounds studied here can be listed in the following order.



With his mixture of model compounds on a sulfided $CoMo/Al_2O_3$ catalyst, Rollmann (*7*) reported that quinoline, *o*-ethylphenol, 2-phenylphenol, indole, benzofuran, and *o*-ethylaniline had first-order rate constants very similar to one another, varying within a factor of only about 1.5 between extremes. *p*-Cresol and 4-propylphenol were considerably more reactive and dibenzofuran significantly less reactive. In contrast, our results indicate that *o*-ethylphenol and *o*-ethylaniline are somewhat more reactive than benzofuran and quinoline, but the previous discussion makes it evident that such generalizations need to be viewed with care.

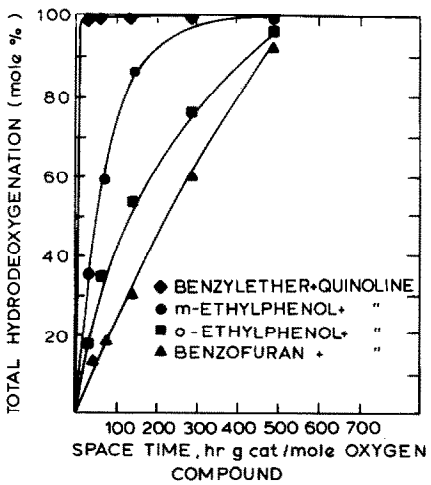


FIG. 14. Relative reactivity of four oxygen compounds in presence of quinoline.

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