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HDN Activities of Methyl-Substituted Quinolines

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The hydrodenitrogenation (HDN) reactivities of quinoline (Q) and several methyl-substituted quinolines (MQ) were determined over a $NiMo/Al_2O_3$ catalyst and a $CoMo/Al_2O_3$ catalyst using a fixed-bed reactor at 613 K and 3.1-MPa pressure. Compared to Q, HDN conversions were about the same when methyl groups were on the aromatic ring, but they were substantially lower for methyl groups on the N-ring, except for 2-MQ. The CoMo catalyst was somewhat more active than the NiMo catalyst. All MQs and Q rapidly reached equilibrium between the Q and the 1,2,3,4-tetrahydroquinoline (THQ1) methyl analogs. It was found that total and HDN activities were roughly related to their respective equilibria, except for 2-MQ, in which the methyl group provides a positive influence. The intrinsic rates of hydrogenolysis of the THQ1s to *o*-propylamines were correlated with the electrostatic potential at the nitrogen atom in the respective THQ1 molecule, most likely related to the adsorptive affinity or reactive affinity on the active site.

Key Words: **quinoline; methyl-substituted quinoline; hydrodenitrogenation (HDN); NiMo catalyst; CoMo catalyst; electrostatic potential.**

INTRODUCTION

Catalytic hydrotreating has become an important process for removal of sulfur and nitrogen from petroleum due to increasing environmental constraints. Heterocyclic compounds containing sulfur and nitrogen are relatively stable structures because the S or N atoms are multiply bonded to their neighbors. Even though the hydrotreating process removes sulfur and nitrogen simultaneously, nitrogen compounds are more resistant than sulfur compounds and require more-severe reaction conditions.

A number of studies have been reported on the effect of methyl group substitution on the hydrodesulfurization of model compounds such as thiophene (1), benzothiophene (2, 3), and dibenzothiphene (3–6). In these studies, it was found that methyl groups on C atoms adjacent to the S atom resulted in lower activity. It is generally believed that the lower activity is caused by steric hindrance to adsorption through the S atom to a catalytic site. Recently, Meille *et al.* (7) reported that the lower activity was due not to adsorption but to different reaction rates. However, it has not been confirmed that this applies for nitrogen-containing compounds because of the greater basicity of the N atom compared to that of the S atom. Indeed, Miciukiewicz *et al.* (8) showed much lower adsorption for a number of N compounds when a methyl group was adjacent to the N atom.

Only limited studies have been reported on the effect of alkyl substituents on HDN reactivity of model N heteroatom compounds. The effect of methyl substituents on the HDN of cyclic five-membered nitrogen compounds has been reported for methyl-substituted indoles (9), where no steric effects were found. For methyl-substituted carbazoles, Wiwel *et al.* (10) found the order of reactivity to be carbazole > 3-methylcarbazole > 2-methylcarbazole > 4-methylcarbazole ~ 1-methylcarbazole, and Dzidic *et al.* (11) found 1-methylcarbazole least reactive, indicative of steric hindrance.

In the case of cyclic six-membered nitrogen compounds compounds, Cerny (12) reported that the effect of methyl groups on hydrogenolysis of methyl-substituted pyridines followed in the series pyridine > 2-methylpyridine > 2,6-dimethylpyridine > 2,4,6-trimethylpyridine, and Dzidic *et al.* (11) found that alkyl groups in the 2- and 6-positions greatly retarded reactivity, both indicative of steric hindrance. However, Liaw *et al.* (13) reported the following order of reactivity: pyridine > 2-methylpyridine > 3-methylpyridine; the latter compound should not exhibit steric hindrance if adsorption is through the N atom. They also found quinoline ~4-methylquinoline > 3-methylquinoline. Bhinde (14) reported that the HDN reactivities of 2,6-, 2,7-, and 2,8-dimethylquinoline are comparable to that of quinoline. It is evident that steric effects alone cannot explain the reactivity of six-membered N heterocyclic compounds.

The HDN of heterocyclic nitrogen compounds generally involves the following reactions: (i) hydrogenation of the nitrogen heterorings, (ii) hydrogenation of the aromatic rings, and (iii) C–N bond cleavage (15). Several studies using quinoline as a model compound for the HDN reaction have invoked various reaction pathways involving a sequence of coupled hydrogenation and hydrogenolysis steps (16–19), as shown in Fig. 1. A rapid hydrogenation (HYD) of

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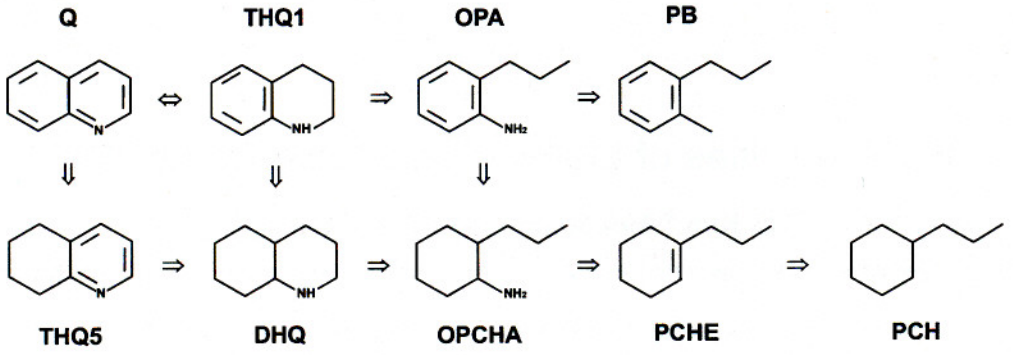
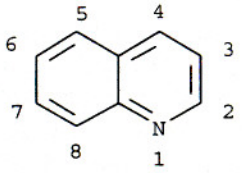


FIG. 1. Simplified reaction network for the HDN of quinoline.

quinoline (Q) to 1,2,3,4-tetrahydroquinoline (THQ1) is followed by two different paths, viz., direct hydrogenation of the aromatic ring to form decahydroquinoline (DHQ), and C–N bond rupture (CNH) to form the intermediate ortho-propylaniline (OPA). An alternate path occurs through hydrogenation of Q to 5,6,7,8,-tetrahydroquinoline (THQ5), followed by hydrogenation to DHQ. The latter, as well as OPA, undergo C–N bond hydrolysis to yield the HDN products propycyclohexene (PCHE), propycyclohexane (PCH), and propylbenzene (PB).

The aim of the present study was to determine the effect of methyl substituents on the HDN of quinoline. The numbering system for the atoms of quinoline is shown in Scheme 1.



SCHEME 1

EXPERIMENTAL

The catalysts used were Topsøe TK-554, which consisted of 4.1% CoO and 20.5% MoO_3 supported on alumina (220 m^2/g), and Topsøe TK-555, which consisted of 3.8% NiO and 24% MoO_3 supported on alumina containing 2% phosphorous (160 m^2/g). The 1.27-mm extrudates were crushed and sieved to 40- to 60-mesh particles. Reactions were carried out in a fixed-bed reactor under vapor-phase conditions at 613 K and 3.1 MPa H_2. A sample of catalyst (0.1–0.3 g), mixed with 5 cm^3 of glass beads, was presulfided with a 10% H_2S–90% H_2 mixture by volume under atmospheric pressure and 673 K for 2 h. The liquid feed consisted of 0.5 wt% quinoline or methyl-substituted quinoline, and 1.0 wt% dimethyldisulfide, in *n*-heptane solvent. All compounds were from Aldrich, at highest purity available. The hydrogen flow rate and liquid flow rate were varied proportionally so that a constant feed concentration was maintained throughout the run. The catalyst was aged with quinoline for 2 days under reaction conditions before proceeding with a run.

Six runs were made, three with each catalyst. Table 1 lists the run conditions. For each catalyst run, different amounts of catalyst were employed, giving different space velocity ranges. At the start of a run, quinoline was first tested at four space velocities (3 h between changes). Then a second compound was introduced for overnight, after which it was tested as before. After all six compounds had been tested, quinoline was again tested to determine catalyst deactivation over a run period of about 300 h. Deactivation was about 5–10%. At the end of Run 1, 1,2,3,4- tetrahydroquinoline was subsequently tested.

Liquid samples taken at various space times were analyzed by gas chromatography (0.32 × 36.6 cm stainless-steel column packed with 6% OV-17 on 100- to 120-mesh WHP Chromosorb) and use of a flame ionization detector and temperature programming of 10°C/min. The identity of individual products was determined by GC/MS analysis (Topsøe A/S) of reaction samples. Molar GC factors were determined using available samples of quinoline and its reaction products. The same relative factors were assumed to apply to the methylquinolines.

All compounds shown in Fig. 1 were determined to be present in reaction samples, including two isomers of PCHE, except for OPCHA (*o*-propylcyclohexylamine), which was not detected. Because Q and THQ1 (and their methyl analogs) rapidly reached equilibrium for all the methylquinolines tested, it was useful to consider the total

TABLE 1

Run Conditions for HDN of Methylquinolines (MQs)

Run	Cat.	Wt. (10^3 kg)	Tau (kg · min/m^3)
1	NiMo	0.285	0.63–1.58
2	CoMo	0.285	0.63–1.58
3	NiMo	0.125	0.28–0.69
4	CoMo	0.125	0.28–0.69

Note. 613 K; 3.5 MPa; 0.339 mol MQ/m^3.

of these two species as reactant. Thus, total conversion (TOT) was defined as the sum of the mole fractions of all compounds, other than Q and THQ1; the HDN conversion was determined in the usual way, i.e., from the sum of the mole fractions of the non-N-containing products. Space–time, tau, was defined as the weight of catalyst divided by the total gas flow (hydrogen plus vaporized liquid feed).

Electronic structure calculations were performed as detailed in a previous publication (9). These calculations allowed us to determine the electrostatic potential (EP) at each atom.

RESULTS AND DISCUSSION

Figure 2 displays the product distribution versus space time for the HDN of quinoline with the CoMo catalyst. Runs A-6 and A-7 were combined to give a larger space–time range. It is seen that the concentrations of all the species in Fig. 1 go through maxima with space–time, indicating they are intermediates in the reaction, except for PCH, which is the ultimate HDN product, together with PB (not shown due to its low yields—less than 2 mol%). Similar profiles were obtained for the MQs, although in some cases the maxima were not reached at the highest space time.

In Fig. 3 plots are presented of TOT conversion for the MQs at one space–time (0.69 kg · min/m^3). The error in conversion is estimated at ±0.02 for high values and ±0.01 for low values. TOT conversion, representing the disappearance of Q + THQ1 at equilibruim, is a good measure of the initial reactivity. It is not related to a unique kinetic parameter, involving a combination of reaction steps to further products; i.e., Q → THQ5, THQ1 → DHQ, THQ1 → OPA (Fig. 1). The general trend for the two catalysts are about the same, with certain exceptions. For TOT conversion, the order of reactivity is

$$\text{NiMo} = \text{2-MQ} > \text{4-MQ} > \text{3-MQ} > \text{Q} \sim \text{6-MQ} \sim \text{8-MQ},$$
$$\text{CoMo} = \text{2-MQ} > \text{4-MQ} \sim \text{6-MQ} \sim \text{8-MQ} > \text{Q} \sim \text{3-MQ},$$

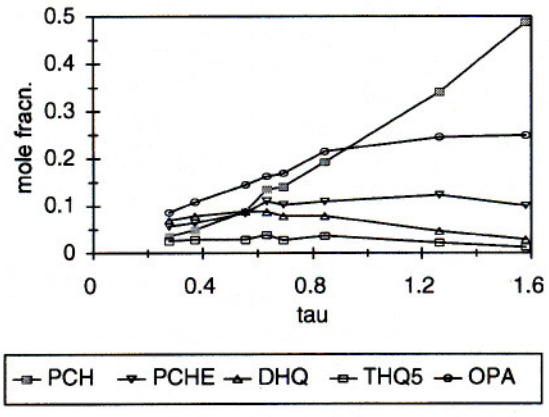


FIG. 2. Product distribution vs space–time (tau) for reaction of Q. Combined Runs 2 and 4.

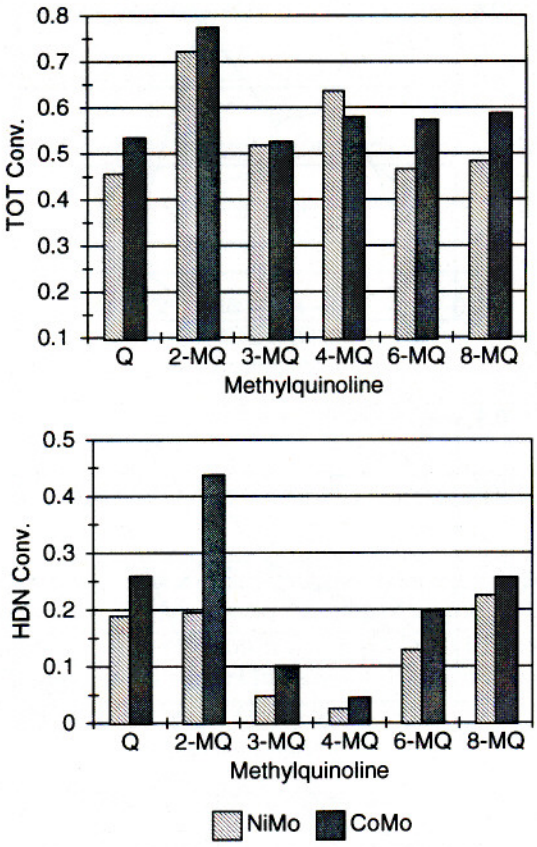


FIG. 3. Total and HDN conversions for Q and MQs at tau = 0.69. Runs 3 and 4.

showing a slight interchange of 3-MQ with 6-MQ and 8-MQ. Only 4-MQ exhibits a higher TOT conversion for the NiMo catalyst, the other MQs and Q being equal or higher for the CoMo catalyst.

Figure 3 also presents HDN activities of the MQs under the same conditions. These are given because HDN represents the ultimate usefulness of the catalyst to produce the desired non-N compounds. Again there is no single parameter representative of HDN due to the many steps involved in obtaining non-N products (Fig. 1). For HDN, the order is given by

$$\text{NiMo} = \text{8-MQ} > \text{Q} \sim \text{2-MQ} > \text{6-MQ} > \text{3-MQ} > \text{4-MQ},$$
$$\text{CoMo} = \text{2-MQ} > \text{Q} \sim \text{8-MQ} > \text{6-MQ} > \text{3-MQ} > \text{4-MQ}.$$

The order is practically the same for both catalysts, except for the relatively high HDN activity of the 2-MQ with the NiMo catalyst.

There are appreciable differences in responses between TOT and HDN conversions, depending on the location of the methyl group. Thus, except for 2-MQ, a methyl group on the N ring (3-MQ, 4-MQ) results in proportionally lower HDN compared to TOT conversion than does methyl on the aromatic ring (6-MQ, 8-MQ). The reason for these differences is shown in Fig. 4, where the mole fraction of

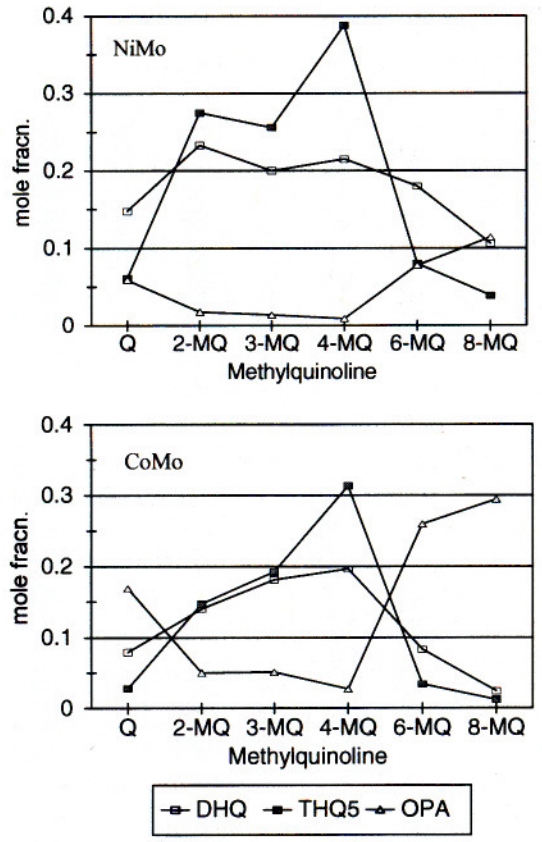


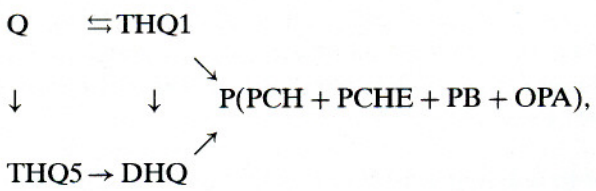
FIG. 4. Yields of N intermediates for Q and MQs at tau = 0.69. Runs 3 and 4.

intermediate N compounds is plotted. (It should be noted here and in subsequent discussions that the products of conversion of MQs will have methyl groups associated with them; thus in Fig. 4, the ratio becomes, for example, 6-MTHQ1/6-MQ. The same applies for the products of the other MQs.) It can be seen that differences between TOT and HDN conversions are mainly due to the larger concentrations of these N intermediates for those compounds in which the methyl group is attached to the N ring. Another difference is the higher intermediate OPA yields for methyl groups on the aromatic ring, while higher THQ5 is produced by methyl groups on the N ring. It is obvious also that substantially more of these intermediates are generated by the NiMo catalyst.

The above results are very similar to those obtained for methyl-substituted indoles under the same reaction conditions (9); that is, with one exception, the same relative total and HDN responses were obtained for methyl groups on the comparable position in quinoline and indole. However, a methyl group in the 2-position (adjacent to the N atom in both cases) gave an increased total conversion for 2-MQ compared to Q, whereas a decreased conversion was found for 2-methylindole compared to indole in the former study. This difference may be due to the fact that quinoline's N atom lone-pair orbital lies in the plane of the ring, whereas in indole, there is no such lone-pair orbital.

Figure 5 displays the ratios of THQ1/Q as a function of space–time for the NiMo catalyst. This ratio remains relatively constant, indicating that an equilibrium between Q and THQ1 is rapidly reached. This was further demonstrated by a run starting with THQ1, which gave essentially the same equilibrium ratio as for Q; i.e., the same ratio was achieved starting from opposite directions. Several researchers have also reported essentially equilibrium between Q and THQ1 under reaction conditions similar to ours (18, 20, 21). The scatter in the plots of Fig. 5 is due to the relatively low values of MQ (<10 mol%), with their attendant error, especially for Q (<4 mol%). Virtually identical results were obtained for the CoMo catalyst. Average equilibrium ratios of THQ1/Q for both catalysts combined are Q = 15.6 ± 1.1, 2-MQ = 3.4 ± 0.2, 3-MQ = 5.5 ± 0.2, 4-MQ = 2.8 ± 0.1, 6-MQ = 8.5 ± 0.6, and 8-MQ = 8.1 ± 1.1. The equilibrium constant is related to this ratio, viz., $K = (\text{THQ1/Q})(1/p_H^2)$. It is seen that methyl groups suppress the equilibrium ratio; those on the N ring exhibit the lowest equilibrium values, those on the aromatic ring are higher, and Q is the highest.

As a consequence of the different equilibria, the path THQ1 → DHQ will be favored for high equilibrium ratios by virtue of the higher concentration of THQ1 prevailing in the these cases, at least early on in the reaction time. Conversely, the path Q → THQ5 will be enhanced at low equilibrium ratios because of the relatively higher prevailing concentration of Q. If we simplify the network as



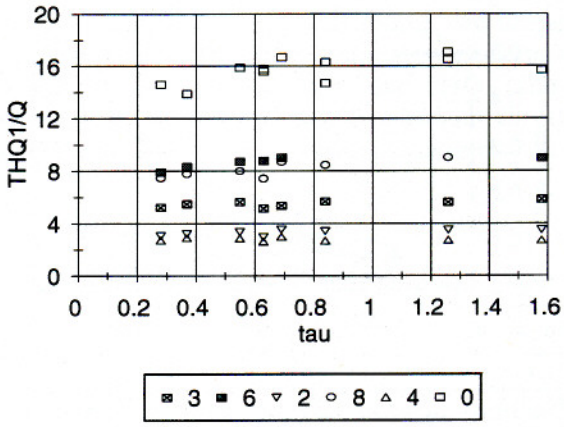


FIG. 5. THQ1/Q ratios vs space–time for Q and MQs. Combined Runs 1 and 3. Numbers refer to methyl position.

then at low space–time, the initial product from Q will be THQ5, and that from THQ1 will be DHQ and P. Thus, the different equilibria that occur at different methyl substitutions will produce different ratios of DHQ/THQ5, as demonstrated in Fig. 6, where the ratio increases regularly with an increase in equilibria. However, DHQ and THQ5 are not in equilibrium, as this ratio generally increased with space–time, as THQ5 is converted to DHQ at higher space–times.

Jian and Prins (22) have proposed four different active sites on NiMo catalysts responsible for HDN. Only two of these are of concern here: a C–N scission (CNH) site for hydrogenolysis reactions, and a hydrogenation (HYD) site for hydrogenation of either the N ring or the aromatic ring. Yang and Satterfield (23) had previously characterized these sites as a Brønsted acid site (CNH) and a sulfur vacancy site (HYD).

In a previous paper (9), we related the initial hydrogenation and hydrogenolysis rates for the HDN of methylindoles to the ionization potentials (IP) of the highest occupied molecular orbital (HOMO) and to the electrostatic potentials (EP) on the N atom, respectively. Because the rapid preequilibrium of the Q reaction network (Fig. 1), it was not possible to evaluate the initial hydrogenation rates. However, it was possible to estimate the initial rates of OPA formation from the hydrogenolysis of THQ1 by extrapolating the OPA vs tau data to the origin (tau = 0). The assumption was made that the formation of THQ1 was so fast at small tau that negligible OPA would be formed before THQ1 attained equilibrium. Thus, the initial slope would represent the initial rate of the hydrogenolysis reaction THQ1 → OPA. The validity of this approach was tested by using data from the run with THQ1 as feed, as now OPA is a direct product of reaction of THQ1. The initial rate of OPA formation was found to be within 10% of that obtained with Q as feed. The initial rate based on

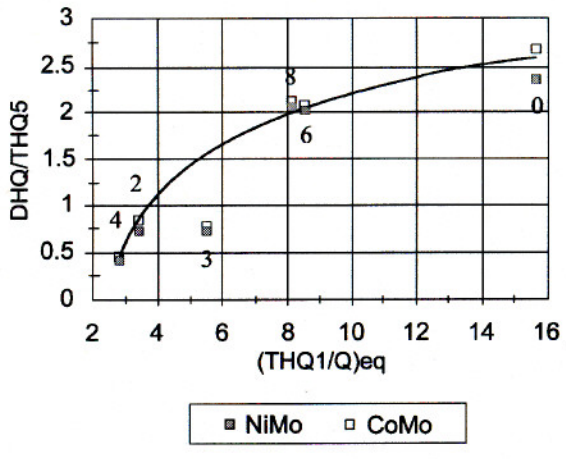


FIG. 6. DHQ/THQ5 ratios vs average THQ1/Q equilibrium ratios at tau = 0.28. Runs 3 and 4.

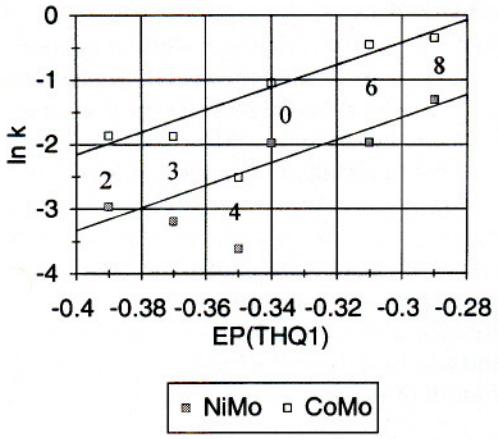


FIG. 7. Relationship between rate constants for OPA formation and electrostatic potentials (EP) of THQ1 and their methyl analogs.

mole fraction of OPA formed includes a contribution from equilibrium; i.e., it depends on the mole fraction of THQ1 at equilibrium. A correction for this needs to be made in order to assess the intrinsic kinetics of OPA formation. Assuming pseudo-first-order kinetics, the initial rate is given by

$$r_o = k[\mathrm{THQ1}]_{eq},$$

where k is the rate constant and the mole fraction of THQ1 is

$$[\mathrm{THQ1}]_{eq} = [\mathrm{THQ1/Q}]_{eq}/(1 + [\mathrm{THQ1/Q}]_{eq}).$$

Then k is given by $r_o/[\mathrm{THQ1}]_{eq}$.

A plot of ln k versus EP for the different methyl groups is shown in Fig. 7, where the EP values are for the N atom of the appropriate THQ1 molecule. Plotting the data as a function of the EP is based on the assumption that the reaction proceeds when the lone-pair electrons on the N atom are coordinated to the active CNH site. Compared to the parent compound, the EP values for methyls on the aromatic ring are higher (less negative), while those on the N ring are lower (more negative). A good correlation for both catalysts is observed, except for 4-MQ. The correlation may be related to the adsorptive affinity or the reactive infinity of the individual THQ1s on the CNH site.

CONCLUSIONS

Significant differences in HDN reactivities of methylquinolines (MQ) were found, depending on the location of the methyl group. Compared to quinoline (Q), total conversion of Q plus 1,2,3,4-tetrahydroquinoline (THQ1) was generally unaffected by methyl groups on the aromatic ring (6- and 8-MQ), whereas methyl groups on the N ring (2- and 4-MQ) gave higher total conversion. For HDN activity,

again methyl groups on the aromatic ring gave about the same conversion as for quinoline, while methyl groups on the N ring gave considerably lower HDN conversions, except for 2-MQ, which was higher. Results were essentially the same for the NiMo and CoMo catalysts.

All MQs and Q rapidly reached equilibrium between Q and THQ1 (and their respective methyl analogs). It was found that total and HDN activities were roughly related to their respective equilibria, except for 2-MQ, in which the methyl group provides a positive influence.

The rate constants for the formation of OPA from THQ1 were found to correlate well with the electrostatic potential on the N atom of the respective THQ1s.

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