

**THE REDUCTION OF NITROGEN- AND SULFUR-CONTAINING
HETEROAROMATIC COMPOUNDS IN A BIPHASIC MEDIUM USING A GROUP
VIII HYDROSOLUBLE ORGANOMETALLIC COMPLEX**

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ABSTRACT

Two-phase hydrogenation of heteroaromatic compounds such as quinoline (Q) and benzothiophene (BT) were performed using as catalytic precursor a mixture of ruthenium trichloride and an excess of the water-soluble ligand *m*-sulfonatophenildiphenylphosphine, in its sodium salt form (TPPMS). The products obtained from the hydrogenation were 1,2,3,4-tetrahydroquinoline (THQ) and dihydrobenzothiophene (DHBt), respectively.

The initial rate of hydrogenation for benzothiophene is enhanced in the presence of quinoline. Other organic nitrogen bases such as aniline, acridine, tetrahydroquinoline, piperidine and triethylamine were also important as promoters in the hydrogenation of benzothiophene. Understanding novel upgrading processes in fuels is the quest for this investigation.

1. INTRODUCTION:

Sulfur and nitrogen-containing aromatics are major contaminants in petroleum derived fuels (e.g., Naphtha, Diesel, etc.). Thiophene (Th), benzothiophene (BT) and derivatives are the most abundant sulfur aromatics in fuel. Quinoline (Q) and other related species represent the main nitrogen-containing aromatics [1]. New legislation represent a threat to these highly refractory compounds because they have to be reduced severely to comply with quality product standards. Degradation of these compounds is carried out via hydrotreating like HDS and HDN; however, limitations in heteroaromatic reduction severely affect upgrading [2].

Industrial HDS and HDN are generally carried out together with many other reactions such as aromatic saturation, olefin hydrogenation, hydrocracking, etc. [1]. Some of these side-reactions are desirable (e.g. regioselective aromatic saturation) because it permits a rational transformation of other undesirable products (polyaromatics). The ability to understand and eventually control hydrotreating reactions may lead to highly selective ways of either removing contaminants for continuing downstream processes or improving the quality of the hydrocarbon itself (e.g. transformations of two-rings fused aromatics into alkyl monoaromatics, helping octane and avoiding smoke in fuel combustion).

To understand the actual mechanistic details in hydrotreating, one could study the selective hydrogenation or hydrogenolysis of heteroaromatic compounds in a homogeneous medium [2]. It will be interesting to investigate whether the rupture of the C-S and C-N bonds (hydrogenolysis) occurred prior or subsequent to the hydrogenation of the heterocyclic rings on solid catalysts. While this information is unknown, it is believed that is much easier to remove sulfur and nitrogen once the aromatic rings have been reduced via hydrogenation [2]. Selective hydrogenation could shed light on novel upgrading in hydrotreating.

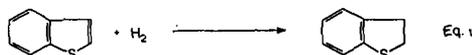
A way to go is the use of transition metal complexes, because they may be characterized by spectroscopic techniques that are much easier to comprehend and handle [2]. Several late transition metal complexes are known to catalyze the regioselective homogeneous hydrogenation of BT and that of Q, and the mechanisms of such reactions have been investigated in detail [3, 4]. Nevertheless, separation problems commonly encountered in homogeneous processes make this approach unattractive for application in petroleum-derived fuels [5,6]. To overcome this problem, the selective hydrogenation step could be done using liquid biphasic catalysis [7]. In this case, the catalytic active species is immobilized in one of the two liquid phases (e.g., water), with the reactants and products maintained in the other (Naphtha); thus allowing a continuous flow process design and better understanding of the different steps involved [8].

2. EXPERIMENTAL:

All manipulations were carried out using standard Schlenk technique, under dry argon or nitrogen. Solvents were purified by conventional procedures. Catalytic runs were performed in an autoclave (PARR, 300 ml, SS-316) with internal stirring and temperature controller. The hydrogenation conditions were 130°C, 69 bar, 613 rpm, S/C, 50:1. Products were analyzed via GC and GC-MS against authentic samples, when available. TPPMS was prepared following published procedure [9].

3. RESULTS AND DISCUSSION:

3.1 Hydrogenation of BT



When a water solution of ruthenium trichloride hydrated and excess TPPMS was placed in a reactor together with a decaline solution of BT, under hydrogenation reaction conditions, the catalytic transformation of BT to DHBT was observed soon after the first hour of reaction (Eq. 1). Two experiments were carried out to establish the responsibility of ruthenium in the catalysis:

- (i) Addition of elemental mercury to the reaction mixture did not affect the catalysis [10].
- (ii) A thermally decomposed aqueous solution containing RuCl_3 and TPPMS yielded a Ru metal suspension which was found to be inactive toward BT hydrogenation under the same reaction conditions.

The initial turnover rate for the conversion of BT to DHBT was $2.9 \text{ mol (mol Ru)}^{-1}\text{h}^{-1}$. For comparison, the homogeneous hydrogenation of BT using $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ as the catalyst precursors proceeded with initial turnover frequencies of 6.1 and $2.2 \text{ mol (mol Ru)}^{-1}\text{h}^{-1}$, respectively, under more stringent conditions (170°C, 110 bar H_2) [3a].

As expected for a reaction at an interface, the stirring rate has a strong influence on the rate of hydrogenation, which went from 30% conversion to 70% conversion, after 18 h, on going from 200 rpm to 600 rpm under the conditions described above [11]. The catalytic solutions were recycled up to four times under strictly anaerobic conditions and used to hydrogenate fresh BT in decaline, without any apparent loss of activity. In contrast, a solution exposed to air after the first hydrogenation run was completely inactive for further hydrogenation.

When the biphasic hydrogenation of BT is carried out in the presence of a nitrogen base (1:1 molar ratio with respect to TPPMS), the initial turnover rate is enhanced. Fig. 1 shows typical reaction profiles in the presence of bases such as quinoline (Q) and aniline (An) in comparison with a non base promoted (NB) reaction. From the lineal part of the curves, maximum turnover frequencies can be estimated at 10.2 and $10.4 \text{ mol (mol Ru)}^{-1}\text{h}^{-1}$ for Q and An, respectively. The basicity of aniline ($p_{\text{Kb}} 9.3$) resembles that of Q ($p_{\text{Kb}} 9.1$). This may be a good reason for the apparent behavior. However, Q plays also a role as phase transfer and emulsion stabilization agent.

Other nitrogen bases such as acridine (Ac, $p_{\text{Kb}} 8.4$), piperidine (Pp, $p_{\text{Kb}} 2.9$) and triethylamine (Tea, $p_{\text{Kb}} 2.9$) can also enhance the rates of BT hydrogenation to the various degrees presented in Fig. 2. The base neutralizes the HCl that is formed in the heterolytic cleavage of H_2 during formation of the catalyst precursor [3e].

3.2 Hydrogenation of Q



Quinoline acts as a co-catalyst in the hydrogenation of BT and it is also hydrogenated to THQ (Eq. 2). Under the same reaction conditions, the hydrogenation of Q is faster than that of BT. The initial turnover rate for this reaction was 78 mol (mol Ru)⁻¹h⁻¹, compared with 2.9 mol (mol Ru)⁻¹h⁻¹ for BT (27 times less active). Organic bases do not influence the initial rate. However, increasing hydrogen pressure has a positive influence in the hydrogenation. In fact, most of the studies on the biphasic hydrogenation of Q were carried out at 35 bars in order to determine more accurately the initial turnover rate (35 mol (mol Ru)⁻¹h⁻¹).

3.3 Catalytic species in aqueous solutions

In the absence of the base, RuCl₃·3H₂O reacts with excess TPPMS in water or methanol to yield [RuCl₂(TPPMS)₂]₂, which in turn reacts with hydrogen to produce the hydride [RuHCl(TPPMS)₂]₂. The latter complex is broken, for instance by cinnamaldehyde leading to an active catalyst for the regioselective hydrogenation of the carbonyl (C=O) bond of CA [12]. In agreement with this, the major Ru-containing products isolated from the aqueous phases after BT hydrogenation in presence of Q or An were characterized by ¹H and ³¹P{¹H} NMR spectroscopy as the complexes RuHCl(TPPMS)₂L₂ (L = THQ, **1** and An, **2**).

Complexes **1** and **2** were independently synthesized by reaction of [RuHCl(TPPMS)₂]₂ with an excess of THQ or An in water, and characterized by NMR and FAB/MS [13].

A fresh sample of **1** was used in the hydrogenation of Q (35 bars, 135°C, 3 h) given the profile observed in Fig. 4 (P1). The water solution was carefully worked up under anaerobic conditions and the brown solid obtained was characterized by NMR, after the catalysis (signals were identical to the fresh catalyst). The complex was redissolved in water and reused in the catalysis of a fresh decaline solution of Q, given the profile P2. This work is a clear indication of the recycle capacity of the complex; which must have a structural relationship with the catalytic active species formed when ruthenium halide reacts with excess TPPMS in the presence of an organic base.

Since both complexes **1** and **2** are coordinately saturated, they are probably not the ones directly involved in the catalysis, but a stabilized form of the actual catalyst, which could conceivably be the corresponding 16-electron species "RuHCl(TPPMS)₂L". Further mechanistic studies are in progress and will be reported elsewhere.

4. CONCLUSIONS:

The regioselective hydrogenation of BT and Q was achieved using a biphasic (water/decaline) catalytic system comprised by ruthenium trichloride and excess *meta*-sulfonatophenyldiphenylphosphine (TPPMS). The hydrogenation of BT is influenced by the addition of organic nitrogen bases as co-catalysts; the order of hydrogenation being: An ≈ Q > Ac > THQ > Pp > Tea. Species of the type HRuCl(TPPMS)₂L₂ (L = An, THQ) have been isolated from the aqueous solutions after the hydrogenation. These species were also obtained using preparative procedures and characterized by NMR and FAB/MS. The tensoactivity of the TPPMS ligand and the phase transfer character of the base are important in the transformation of BT under biphasic conditions. Novel upgrading process of petroleum fuel is the main quest of the work presented.

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- [13] Data for complex 1: ^1H NMR (CD_3OD), THQ: 5.62 (t, $J=5.7$ Hz, H_2), 4.38 (t, $J=6.6$ Hz, H_3), 5.14 (t, $J=5.7$ Hz, H_4), 8.30 (s, H_5), 8.33 (s, H_6), 8.51 (s, H_7), 8.55 (s, $\text{H}_{3,8}$), -10.30 (t, $J_{\text{H-P}}=36$ Hz, Ru-H), 8.11 - 7.10 (M, ppm). ^{31}P (^1H) NMR system δA 60.38; δM 57.57 ($J_{\text{P-P}}=35$ Hz). Data for complex 2: ^1H NMR (CD_3OD), 8.37 (m, aniline), 5.43 (t, $J=6$ Hz, NH_2), -10.18 (t, $J_{\text{H-P}}=37$ Hz, Ru-H), 8.11-7.10 (m, TPPMS). ^{31}P (^1H) NMR: 57.9 (s). FAB-MS (m-nitrobenzyl alcohol) (Z/E): 1122 [RuHCl(TPPMS) $_2$ (An) $_2$] + H; 996 [RuHCl(TPPMS) $_2$ (An)]+H; 941 [RuHCl(TPPMS) $_2$] + H; 902 [Ru(TPPMS) $_2$] + H; 880 [Ru(TPPMS) $_2$ Na] + H; 400 [TPPMS-Na 2H $_2$ O].

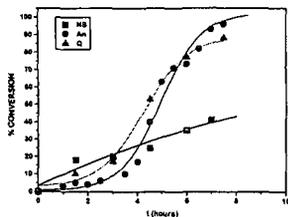


Fig. 1 Profile for the biphasic hydrogenation of BT. NB, No base added, An, aniline and Q, quinoline.

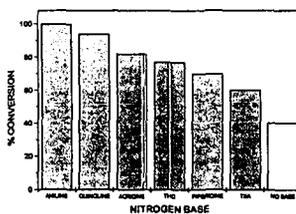
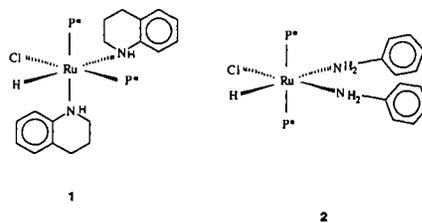


Fig. 2 Influence of basicity in the biphasic hydrogenation of BT with RuCl_3 and TPPMS.



$P^* = \text{TPPMS} = (\text{C}_6\text{H}_5)_2\text{P}(m\text{-C}_6\text{H}_4\text{SC}_3\text{Na})$

Fig. 3. Structures of aqueous organometallic species characterized during the reaction of RuCl_3 , excess TPPMS and THQ or An.

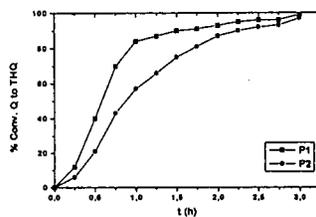


Fig. 4. Profiles for the biphasic hydrogenation of Q using the same catalyst, but two fresh solutions of Q in decaline.