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Journal of Hazardous Materials B74 (2000) 187–195

**Journal of
Hazardous
Materials**

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Decomposition of isoquinoline and quinoline by supercritical water

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Received 29 March 1999; received in revised form 28 December 1999; accepted 3 January 2000

Abstract

The ability of supercritical water (SCW) to decompose heterocyclic compounds (quinoline and isoquinoline) has been explored in this study. The results obtained suggest that water acts as a chemical reagent above its critical point (374°C and 22.1 MPa). Significant proportions of isoquinoline and quinoline were removed during the reaction with SCW. The response of these compounds to pyrolysis was also compared with their reaction with SCW. Both compounds were relatively more reactive in the presence of SCW than during pyrolysis. Because of the different positions of N atom in the two compounds, they reacted with SCW differently. Breaking of C–N bonds during SCW reaction was by hydrogenation and hydrocracking, while pyrolysis was due to thermocracking mainly. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical water; Quinoline; Isoquinoline; Heterocyclic compounds

1. Introduction

Heterocyclic compounds such as quinoline, isoquinoline and benzothiophene are frequently encountered in the environment because of their presence in fossil and synthetic fuels (oil shales, coal, oil sands and shale oils) and some pesticide mixtures, such as creosote. Due to the presence of S and N in heterocyclic compounds, they are receiving increasing attention as a result of the health risks posed by these compounds. The use of supercritical water to convert hazardous organic compounds to less hazardous compounds such as carbon dioxide and water has been reviewed by Paulatis et al. [1], Shaw et al. [2], Tester et al. [3], and Gloyna and Li [4]. Under supercritical

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conditions, fluids behave like dense gases with high diffusivities [5], resulting in high mass transfer. This has allowed supercritical fluids (SCF) to dissolve non-volatile compounds more easily. It has been reported that the reaction during supercritical fluid extraction varies from gas-like to liquid-like as the solvent density increases (Townsend et al. [6]). It would, therefore, be reasonable to expect two different reaction pathways, depending on density. Dielectric constant and ion product of supercritical water (SCW) are some of the properties that are responsible for its solvent power. At room temperature and atmospheric pressure the ion product is 1×10^{-14} (mol/l)², but at high pressure and temperature, the ion product increases significantly. For example, in the vicinity of 34.5 MPa and 300°C, the hydrogen ion concentration will be 3×10^{-6} mol/l, this is an increase of about 30 times the concentration at room temperature and atmospheric pressure. The dielectric constant of SCW ranges from 2 to 30, which is similar to the range from a nonpolar solvent such as hexane (with dielectric constant of about 1.8) to a polar solvent such as methanol (dielectric constant of 32.6). With the ion product and dielectric constant, SCW possesses the effect of an acid catalyst and the ability to dissolve organic substances that do not dissolve in water under room temperature and atmospheric conditions. To assess the reaction and solvent effect of SCW with isoquinoline and quinoline, these compounds were pyrolyzed at 400°C and 22.1 MPa.

This paper describes the reactions of quinoline and isoquinoline in the absence and in the presence of supercritical water in order to better understand their behavior during SCW oxidation of hazardous materials in which they are present. The knowledge obtained from this study will also provide some understanding of the reaction of similar heterocyclic compounds in the presence of supercritical water.

2. Materials and experimental procedures

2.1. Samples

Reagent-grade isoquinoline and quinoline were obtained from Aldrich Chemical and used as received without further treatment.

2.2. Experimental

All reactions were carried out in a 10 ml (13 cm long, 9 mm i.d.) microbomb fabricated from 316 stainless steel tubing with 3 mm wall thickness. The bomb was sealed at one end with a cap and the other connected to 0.635 cm o.d. tubing which was fitted with a valve for pressurizing the reactor and venting the gas, as well as pressure gauge for monitoring the reaction pressure.

In each run, the micro reactor was loaded with approximately 1.0 g of solid sample or 2 ml of liquid sample, and 3.2 ml of water was added to the reactor. After loading and closing the reactor, nitrogen was used to purge the reactor before pressurizing the system to approximately 14 MPa, which generated the required hot pressure of 22.1 MPa (3200 psig). The reactor was then immersed in a preheated fluidized sand bath and the time of

immersion recorded as the start of the experiment. The reaction temperature was maintained at 400°C in all the runs. In addition, the reaction of quinoline with SCW was carried out in the presence of approximately 0.06 g Fe₂O₃ as catalysts. The reactions were carried out at 400°C, 22.1 MPa (3200 psia) pressure, and 48 h residence time.

During each run, the reactor was agitated by up and down motion at approximately 120 cycles/min. After completion of the experiment, the reactor was removed from the sand bath and quenched in cold water. Gaseous products were then collected by water displacement. The reactor was opened and its contents collected by washing with tetrahydrofuran (THF). THF was removed by evaporation, this was achieved by leaving the products in a fume hood until the weight of the sample was constant. The aqueous and organic phases were recovered in a separating funnel, and solid residues if present, were removed by filtration.

The gaseous products were analysed by gas chromatography (GC), while liquid products were analysed by gas chromatography–mass spectroscopy (GC/MS). Ammonia gas generated during the experiments entered the aqueous phase to form ammonium, which was determined quantitatively by ion specific electrodes.

The preliminary analysis of the liquid products was conducted on a Varian model 3700 Gas Chromatograph equipped with (30 × 0.53 mm) 5 μm DB-1 megabore capillary column and thermal conductivity detector in a temperature programming mode. The GC/MS data were obtained using VG 70 E mass spectral and Varian Vista 600 equipped with (30 × 0.25 mm) 1.5 μm DB-1 megabore capillary column and a flame ionization detector. The quantity of each gaseous product was determined by comparing the peak area of the spectrum with that of a standard sample of known concentration.

Mass spectra were identified by comparison with library records. The extent of reaction and amount of reaction products were estimated by comparing the peak areas for the spectra of unreacted model compound with the peak areas for the spectra of the residual model compounds in the reaction product mix.

3. Results and discussions

Tables 1 and 2 show the GC/MS distribution of the dominant liquid products from pyrolysis and SCW interaction of isoquinoline and quinoline.

The product distribution obtained from GC/MS analyses was used in developing some reaction sequences during SCW destruction of the heterocyclic compounds. According to the results on these tables, quinoline is more reactive than isoquinoline. During quinoline reactions more products were produced (Table 2). Table 1 shows only a slight difference in reaction products obtained for isoquinoline pyrolysis and hydrolysis.

Figs. 1–4 outline the plausible major reaction paths as inferred from GC/MS data. These possible reaction paths suggest that both compounds react.

3.1. Isoquinoline

Table 1 shows the GC/MS distribution of dominant liquid products from supercritical water reaction and pyrolysis of isoquinoline.

Table 1
Reaction products from isoquinoline pyrolysis and hydrolysis

Product	Formula	MW	Pyrolysis	(SCW)Hydrolysis
<i>Yields (wt.%)</i>				
Unreacted			86.0	83.7
Reaction products ^a			1.5	3.6
Unaccounted for ^b			12.5	12.7
<i>Composition of reaction products (wt.%)</i>				
Toluene	C ₇ H ₈	92	–	trace ^c
<i>O</i> -xylene	C ₈ H ₁₀	106	–	17.9
Ethylbenzene	C ₈ H ₁₀	106	–	18.3
Benzene, 1,3 dimethyl	C ₈ H ₁₀	106	–	trace
Benzene, 1-ethyl-2-methyl	C ₉ H ₁₀	118	31.0	21.2
Benzene, 1-ethyl-3-methyl	C ₉ H ₁₂	120	–	21.2
Naphthalene, 2-methyl	C ₁₁ H ₁₀	142	69.0	–
Benzo F quinoline	C ₁₃ H ₉ N	179	–	20.9
5H-indo 1,2- <i>b</i> -B pyridine	C ₁₂ H ₉ N	169	–	trace

^aNot including gases.

^bPossibly contained in product gases.

^c< 0.1%.

Table 2
Major products from quinoline pyrolysis and hydrolysis

Product	Formula	MW	Pyrolysis	SCW (Hydrolysis)
<i>Yields (wt.%)</i>				
Unreacted			77.3	31.6
Reaction products ^a			13.4	53.5
Unaccounted-for ^b			9.3	14.9
<i>Composition of reaction products (wt.%)</i>				
Aniline	C ₆ H ₇ N	93	–	9.2
Toluene	C ₇ H ₈	92	–	3.2
<i>O</i> -xylene	C ₈ H ₁₀	106	–	31.2
Benzene, ethyl methyl	C ₉ H ₁₀	118	–	0.6
Benzenamine 2-methyl	C ₇ H ₉ N	107	–	11.2
Benzenamine, 4-ethyl	C ₈ H ₁₁ N	121	–	19.6
Benzenamine, 4-methyl	C ₇ H ₉ N	107	10.4	–
Quinoline, 1,2,3,4-tetrahydro	C ₉ H ₁₁ N	133	3.0	–
Naphthalene, 2-methyl	C ₁₁ H ₁₀	142	19.4	–
Hydroxy-quinoline	C ₉ H ₇ NO	145	–	9.7
Quinoline, ethyl	C ₁₁ H ₁₁ N	157	14.2	–
Quinoline, methyl ^c	C ₁₀ H ₉ N	143	26.1	3.6
Quinoline dimethyl ^c	C ₁₁ H ₁₁ N	157	–	9.3
Naphthalene dimethyl	C ₁₂ H ₁₂	156	–	2.4
2,2-Biquinoline	C ₉ H ₇ NO	145	26.9	–

^aNot including gases.

^bPossibly contained in product gases.

^cIsomers.

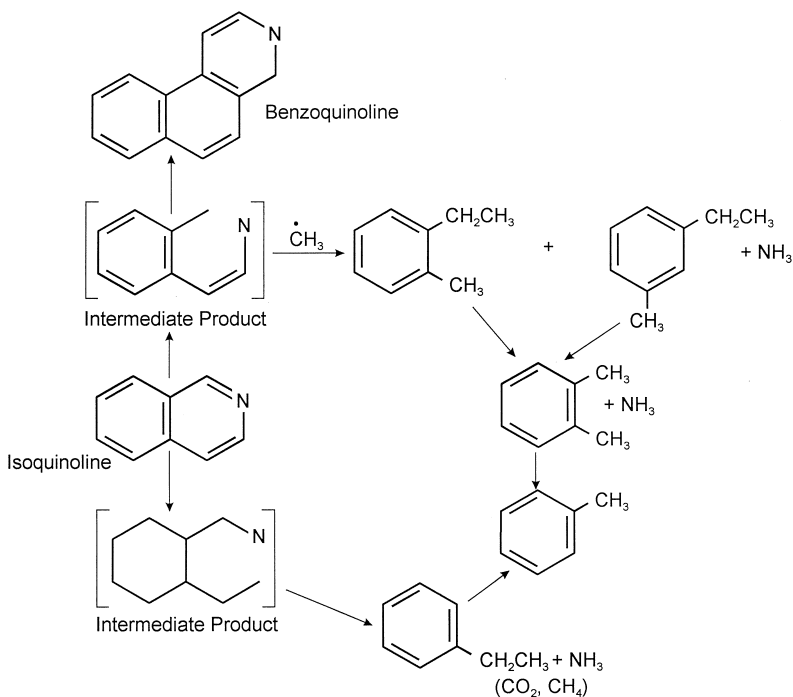


Fig. 1. Possible reaction sequence for SCW–isoquinoline interaction.

The reaction sequence in the presence of SCW is outlined in Fig. 1. The lower molecular weight compounds generated during the reaction of isoquinoline with supercritical water suggests that SCW is active as a reactant during thermal degradation. Most

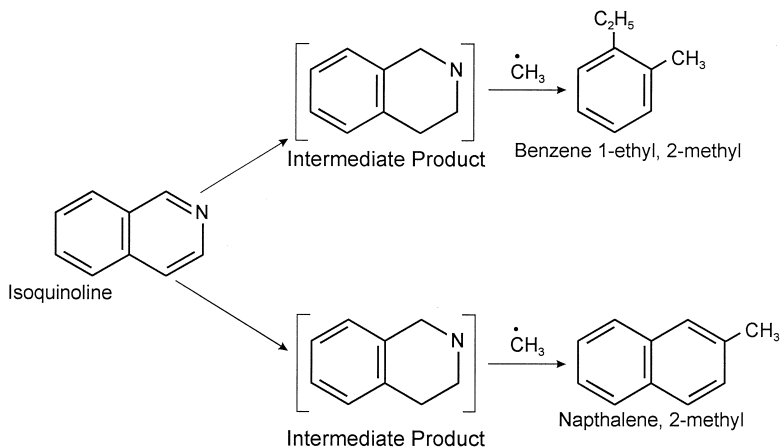


Fig. 2. Possible reaction sequence for isoquinoline pyrolysis.

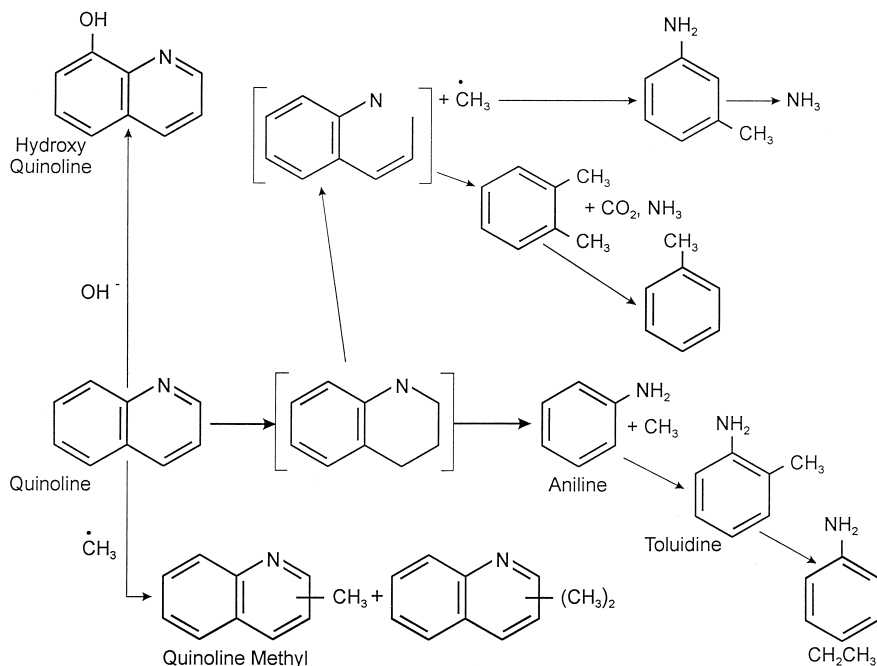


Fig. 3. Possible reaction sequence for SCW–quinoline interaction.

of the generated products are alkyl benzenes which account for over 70% of the major products; this suggests that SCW donated protons that saturated heterocyclic rings which consequently generated alkyl radicals such as $\cdot\text{CH}_3$ and $\cdot\text{CN}$. The implication is that heterocyclic rings are more reactive than homocyclic rings. Similar sequences of reactions has been observed by Houser et al. [7]. The presence of ammonia in the gaseous products, also supports a role of SCW in donating proton for converting N to NH_3 . Figs. 1 and 2, respectively outline the possible reaction sequence for isoquinoline SCW interaction and pyrolysis under the experimental conditions used in this study.

Carbon dioxide (CO_2) is a predominant gaseous product resulting from interaction of quinoline and isoquinoline with SCW. This suggests that either quinoline or isoquinoline and/or their reaction products underwent oxidation reaction.

In contrast to isoquinoline–SCW interaction, pyrolytic reaction of isoquinoline generated fewer products of higher molecular weights. Only two products, benzene, 1-ethyl-2-methyl and naphthalene, 2-methyl are the major identified products when isoquinoline was pyrolyzed.

A proposed overall reaction scheme for isoquinoline pyrolysis is presented in Fig. 2.

3.2. Quinoline

Table 2 illustrates the distribution of the dominant products from SCW decomposition of quinoline in the presence of Fe_2O_3 as a catalyst. Other experimental conditions were similar to the ones used for isoquinoline.

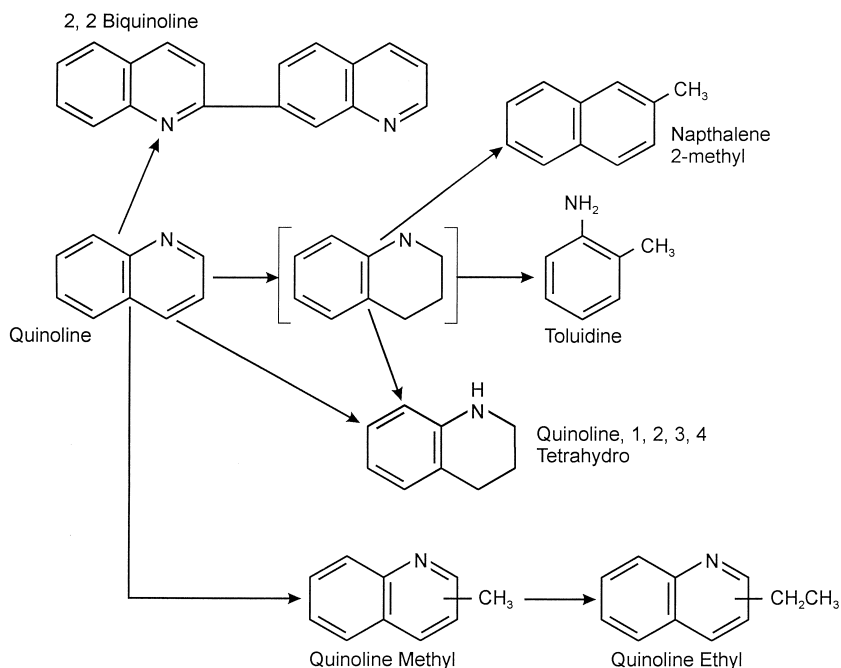


Fig. 4. Possible reaction sequence for Quinoline pyrolysis.

Quinoline did not show any interaction with SCW in the absence of Fe_2O_3 . The product slate (Table 2) allows the inference that free radical capping took place. For instance, the formation of alkyl benzene such as toluene and xylene supports this. Table 1 also indicates that isoquinoline is not as reactive as quinoline. Product slates are different from those of isoquinoline reactions. Possible reaction sequence for interaction between quinoline and SCW is depicted in Fig. 3. Generation of aniline type products has been ascribed by Houser et al. [7] as a result of pronounced preference for 1–2 bond rupture, unlike isoquinoline where both 1–2 or 2–3 bond rupture is possible. The presence of naphthalene dimethyl also suggests that naphthalene is an intermediate product that may arise from methyl–indane interreaction.

Formation of hydroxyl quinoline must have been initiated by ionic reactions that involved H^+ and OH^- ions. Hydrogenation by H^+ enables the heterocyclic ring to be saturated, and this may be followed by hydrogenolysis of C–N bonds that first opens the hetero-ring and then converts the resultant aliphatic and aromatic amine intermediates to hydrocarbons and ammonia (Houser et al. [7]). Also possible is that hydroxyl quinoline is formed by direct attack of OH^- on quinoline.

Similar to isoquinoline pyrolysis, heavier molecular weight compounds were formed during quinoline pyrolysis. Fig. 4 presents the possible products from quinoline pyrolysis. The formation of 2,2-biquinoline suggests that the main reaction mode is thermal cracking, followed by random polymerization to heavier molecules. Although it has been reported that both quinoline and isoquinoline are difficult to pyrolyse, Cocchetto

and Satterfield [8] have shown that quinoline can be readily reduced to dihydroquinoline in the presence of metals and acids; the reaction proceeds via 5,6,7,8-tetrahydroquinoline to 1,2,3,4-tetrahydroquinoline.

Results from this study will help to understand how heterocyclic nitrogen compounds will react during waste treatment by incinerator and SCWO. The implication of the results is that the products distribution from hydrolytic reaction will be more likely to occur during SCWO of waste containing nitrogen compounds, while products from pyrolytic reaction will be similar to the products likely to occur during incineration of nitrogen compound wastes.

4. Conclusions

This study has shown that water is a good solvent for the decomposition of nitrogen heterocyclic compounds. The addition of approximately 0.06 g of Fe_2O_3 was effective in decomposing quinoline by supercritical water.

In general, the extent of reaction is greater during reaction with SCW than in pyrolysis (see Figs. 1–4). This is supported by the lower molecular weight products generated during interaction with SCW. Also, very different product slates were obtained during SCW interaction and pyrolysis. Carbon dioxide is a predominant gaseous product resulting from interaction of quinoline and isoquinoline with SCW. This suggests that either quinoline/isoquinoline and/or their reaction products underwent oxidation reaction. This is expected since it was reported that SCW oxidation is an efficient method for organic waste destruction [9]. It could be inferred that the dominant reactions during SCWE are:

1. Hydrogenation, with H_2 produced from water, and
2. Hydrocracking due to the relatively high reaction temperature.

The result of this study will help in designing a treatment technology for hazardous waste using supercritical fluids.

The addition of carbon monoxide (CO) to the SCW has been reported to enhance the reaction between some fossil fuels and SCW through water gas shift reaction, Ogunsola and Berkowitz [10]. Addition of CO is recommended for future study of heterocyclic compounds reaction with SCW.

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