

DEGRADATION OF QUINOLINE BY WET OXIDATION— KINETIC ASPECTS AND REACTION MECHANISMS

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Abstract—The high temperature, high pressure wet oxidation reaction of quinoline has been studied as a function of initial concentration, pH and temperature. At neutral to acidic pH, it is effective in the oxidation of quinoline at 240°C and above, whereas under alkaline conditions the reaction is markedly slowed down. The results indicate that the reaction is an auto-catalysed, free radical chain reaction transforming 99% of quinoline to other substances. Of the quinoline, 30-50% was oxidised to CO₂ and H₂O depending on the initial concentration. Wet oxidation of deuterium-labelled quinoline was used as a method for verifying and quantifying the reaction products. Fifteen reaction products were identified and quantitatively determined, accounting for 70% of the parent substance. The formation of succinic acid is suggested to be a result of a coupling reaction of the acetic acid radical. A reaction mechanism is suggested for the degradation of quinoline; it involves hydroxyl radicals and the possible interaction with autoclave walls is discussed. © 1998 Elsevier Science Ltd. All rights reserved

Key words-wet oxidation, degradation, aza-arene, quinoline, kinetics, reaction mechanism, succinic acid, mass balance, deuterium labelling

INTRODUCTION

Wet air oxidation is a wastewater treatment process known to break down organic compounds at elevated temperatures and under aqueous conditions. The process is preferably used for treating wastes which are deleterious to biological treatment, e.g. those containing toxic compounds or having high salt concentrations (Randall and Knopp, 1980; Perkow et al., 1981). Tar products originating from gasification and oil shale processing, which are of environmental concern, are typical examples. Quinoline represents a group of PNA-compounds (poly nuclear aromatics), namely the aza-arenes, which are closely related to the polycyclic aromatic hydrocarbons (PAHs). Quinoline is the aza-arene derived from naphthalene. With an N-atom incorporated in the ring system, the water solubility is markedly enhanced; thus, the bio-availability is increased with an accelerated risk to the environment. Quinoline is biologically transformed to 2hydroxyquinoline, whereas further biological processes apparently take place only very slowly (Malmstead et al., 1994). The low biodegradation of quinoline is also reflected in the considerable amounts of quinoline found in ground water from gasification sites (Pereira et al., 1983; Fowler et al., 1994).

matic compounds have been reported for phenol and related water-soluble compounds (Sadana and Katzer, 1974; Willms et al., 1987; Joglekar et al., 1991), trinitrotoluene (Hao et al., 1994), phenanthrene (Larson et al., 1988) and methylpyridines (Allen et al., 1994). All of these studies suggest that hydroxyl radicals play an important role in wet oxidation. Wet oxidation of methylpyridines at subcritical conditions (Allen et al., 1994) and phenol at supercritical conditions (Ding et al., 1995) lead to the conclusion that the oxidation route occurs through two different path ways, namely a dimerization and a ring-opening process. Reaction products from wet oxidation of pyridines compared to products derived from experiments using Fenton's reagent, which is a hydroxyl-radical forming agent (Walling, 1975) brings evidence for the involvement of the hydroxyl radicals in the wet oxidation process (Allen et al., 1994). However, no consideration

Quinoline is well suited for kinetic studies in the wet oxidation process due to its high water solubi-

lity (Table 1) compared to, for example, naphtha-

lene, which is the most water-soluble PAH

compound known (Pearlman et al., 1984). Wet oxi-

dation of mixed tar compounds adsorbed on soil

(Skaarup and Bjerre, 1989) have demonstrated that

quinoline is removed from the soil by the treatment;

however, the complex mixture of tar components

precluded attempts to identify the reaction pro-

ducts. Fundamental studies of wet oxidation of aro-

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Table 1. Physical properties of quinoline			
C.A.S. Reg. No.	91-22-5		
Structure			
Formula	C ₉ H ₇ N		
Molecular weight	129.15		
Melting point	-19.5		

237.7

0.6 g/100 ml

4.95

219,277,301,313 nm

has been made about the formation of the initial concentration of hydroxyl radicals. The many results published concerning wet oxidation are often contradictory, e.g. the oxidation of phenol. Different activation energies have been observed (Willms et al., 1987). Both induction periods and no induction periods have been observed (Devlin and Harris, 1984; Willms et al., 1987). Oxidation and the absence of oxidation in the uncatalysed reaction have also been observed at, respectively, 415 K and 418 K (Sadana and Katzer, 1974; Willms et al., 1987). Besides, there is a general lack of information on mass balances from wet oxidation experiments, probably due to the fact that a large number of oxidation products remain unidentified. Consequently, there is still a need for further basic studies of the reaction mechanisms, in which both catalytic and non-catalytic reactions need to be taken into account (Mishra et al., 1995).

This paper concerns the kinetic and fundamental aspects of wet oxidation of quinoline. Thus, the effects from temperature, initial concentration and pH were investigated. Deuterium-labelled (D_7) -quinoline was used in wet oxidation experiments in order to identify and quantify the reaction products. The results enabled a formulation of a detailed mass balance, and a basis was made for a reaction mechanism.

MATERIALS AND METHODS

Chemicals

Boiling point

pK_a

Solubility in water at 25°C

UV absorbance (methanol) λ_{max}

In all experiments, analytical grade chemicals were used. The quinoline was distilled before use. For pH adjustments sulphuric acid or sodium hydroxide was used.

Wet oxidation experiments

For the wet oxidation experiments, a specially designed autoclave of 2 litres was used; a short heating and cooling profile made it suitable for kinetic studies (Sørensen and Bjerre, 1992). The experiments were carried out by adding 1 litre of distilled water containing 25–250 mg/litre quinoline to the autoclave, then adding 20 bar oxygen to 1 bar of atmospheric air, corresponding to a total pressure of 21 bar in the remaining gas volume of 1 litre. The reaction temperatures were 220–280°C, whereby the pressure increased to 58–76 bar, depending on the temperature. The solubility of oxygen at these conditions were approximately 0.8-1.6 ml-O₂/g-H₂O (Pray *et al.*, 1952). The gasliquid mass transfer was accomplished by mixing with a 137

pumping wheel which ensured a constant tubular flow of the solution through the loop of the autoclave. Thereby, an excellent heat transfer was maintained which resulted in an only 3 min heating-up time and 0.5 min coolingdown time. Kinetic experiments were carried out as follows. Upon reaching the desired temperature, the desired holding time was kept, after which the reactor was cooled in an ice bath; it was then opened and a sample was withdrawn. Following this, the reactor was closed, another supply of oxygen was added and the reactor was again heated to the desired temperature. In that way, samples were taken at appropriate intervals. The holding time did not include the heating and cooling periods. The samples were stored in a refrigerator unless they were analysed immediately. All wet oxidation experiments were conducted in duplicates.

Sample work up for product identification and quantification

For identification/quantification of quinoline, the sample was adjusted to pH 8–9, and a known amount of D_7 -quinoline was added before extraction with iso-octane. For product identification, an aliquot was extracted with ether (2:1) after adjusting pH to 7 by addition of NaOH or H₂SO₄, and the ether fraction was allowed to evaporate at room temperature to a few millilitres (Allen *et al.*, 1994). One wet oxidation experiment was carried out using 100 mg/litre D_7 -quinoline at 260°C. After identifying the products in an ether extract, a new aliquot was extracted with known amounts of non-deuterated labelled compounds used as internal standards. Samples for silyla-tion and esterification were freeze-dried.

- Silylation was performed using bis-(trimethylsilyl)-trifluor-acetamide.
- Esterification was performed by adding methanol and H₂SO₄ (97%) (50:1) to the freeze-dried sample, reflux for 6-8 h; addition of water and sodium carbonate for neutralization was followed by ether extraction.

The products from ether/iso-octane extraction, silulation and esterification were examined by GC/MS.

HPLC

Water samples were analysed by high-performance liquid chromatography (HPLC) with a Perkin Elmer (Norwalk, CT) 250 Binary LC pump and a 253 diode array detector. The reverse-phase column was a Phenomenex (Torrance, CA) Nucleosil5C₁₈, 100Å (250×4.60 mm).

- Quinoline and 2-hydroxyquinoline were analysed with a gradient of methanol in water (46–90%) and monitored at 315 nm.
- Nicotinic acid was analysed using 1% acetic acid in water as eluent and monitoring at 260 nm.
- 2-hydroxynicotinic acid was analysed with a gradient of methanol in water (25–90%, 1% acetic acid, pH:3.20 and monitoring at 325 nm.

GC/MS

Gas chromatography and mass spectrometry (GC/MS) analyses were performed on a Varian (Sunnyvale, CA) Saturn ion trap mass spectrometer. Column, XTI-5 ($30 \text{ m} \times 0.25 \text{ mm}$ i.d); oven temperature, $40^{\circ}\text{C} \rightarrow 325^{\circ}\text{C}$ (20°C/min).

IC

Ion chromatography (IC) was performed on a Dionex (Sunnyvale, CA) 4000i ion chromatograph.

• Low-molecular-weight acids were analysed using 1 mM HCl as eluent and 5 mM tetrabutyl ammonium hydroxide as regenerant; column, HPICE AS1.



Fig. 1. Kinetics of wet oxidation of quinoline as a function of time and temperature. Initial concentration 250 mg/litre quinoline.

 Ammonium, nitrite and nitrate were analysed using 2.7 mM Na₂CO₃, 0.3 mM NaHCO₃ as eluent. Column, HPIC-AS4.

TOC

Total organic carbon (TOC) was determined by means of a Shimadzu TOC-5000: IR-detection after combustion at 680°C (Pt catalyst). Compensation for inorganic carbon was made by acidification.

Metal analysis

Ni was measured by means of HR-ICP/MS.

RESULTS AND DISCUSSION

Temperature and concentration effects

The temperature dependency was examined using an initial concentration of 250 mg/litre quinoline. The effects of temperature were mainly seen in the duration of the induction periods. At 220°C the induction period lasted for 45 min, whereupon quinoline was totally removed within the next 30 min (Fig. 1). The slight decrease in concentration during the induction period was not due to the sampling, as had been found by others (Willms et al., 1987), as these samples were drawn from a cooled reactor; the decrease in concentration could reflect a slow degradation rate of quinoline. At higher temperatures, much shorter induction periods were observed. In the experiments at 240, 260 and 280°C the induction periods were less than 10 min. The remarkable change in the induction periods as the temperature rose from 220 to 240°C shows that a critical temperature exists for the decomposition of quinoline.

The oxidation rates were too high to allow sufficient data to be acquired for meaningful regression analysis. However, the reaction rates appear similar for all four temperatures. The curves are S-shaped, corresponding to an initial low reaction rate, followed by a high reaction rate and terminated by a low reaction rate. Such reactions are considered to be auto-catalytic, meaning that some of the products of the reaction act as a catalyst (Levenspiel, 1972).



Fig. 2. TOC (mg/litre) under wet oxidation of 250 mg/litre quinoline as a function of temperature and time.

Induction periods are most often explained by the time needed for generating a sufficient concentration of free radicals (Willms et al., 1985). As the oxygen pressure was in excess in all experiments the radicals produced must be more reactive than oxygen itself, e.g. hydroxyl radicals as proposed in the literature (e.g. Allen et al., 1994). Induction periods have previously been observed for the oxidation of aromatics, e.g. for the catalysed oxidation of phenol (Willms et al., 1987, Joglekar et al., 1991), m-xylene (Willms et al., 1987) and for the uncatalysed oxidation of phenol (Sadana and Katzer 1974). The induction periods observed for substituted phenols depended on the type and positions of substituents (Joglekar et al., 1991). The reaction course with respect to the induction periods, temperature dependency and shape of the kinetic curves for the oxidation of quinoline show some resemblance to those observed for the decomposition of m-xylene and phenol (Willms et al., 1987). The reaction temperature needed for activating the oxidation is similar only to that observed for *m*-xylene, whereas the reaction temperature is much lower for the decomposition of phenol. On the other hand, the extremely fast reaction phase following the induction periods observed here for quinoline is similar to that observed for phenol.

The TOC measurements follow the quinoline degradation smoothly through the induction periods, but are all delayed with respect to carbon degradation under the rapid reaction phase (Fig. 2). At 280°C and 10 min reaction time, most of the carbon is still measured by TOC, whereas approximately 30% of quinoline has been transformed. At 260 and 240°C and 20 min reaction time only a few mg/litre quinoline is detected but most of the initial TOC is still measured. After 30 min, about 50% of the carbon was oxidized to carbon dioxide and water in both experiments. At this reaction time steady-state levels of TOC are reached and a much slower degradation rate seems to follow (Fig. 2). This may indicate that mainly one cyclic ring is attacked by the treatment and the remaining ring system is difficult to oxidize. As the pyridine ring was expected to be the more stable under the



Fig. 3. Kinetics of wet oxidation of quinoline using three different initial concentrations: 25, 100 and 250 mg/litre quinoline, 260°C.

treatment (Albert, 1968) the reaction products from quinoline degradation were expected to be derived mainly from pyridine and its derivatives (see under "Reaction products").

At 260°C, three levels of quinoline concentrations were studied: 25, 100 and 250 mg/litre (Fig. 3). The results show that the initial concentration of quinoline is of importance for the induction periods and the reaction time needed for a complete removal of quinoline. The higher the concentration the shorter the induction periods and the more complete will be the removal of quinoline. Using 25 mg/litre only 25% removal was observed. It should be noted that, in all experiments, oxygen was added in excess, eliminating possible oxygen deficiencies. Concentration effects as seen here have not previously been reported. On the contrary, Willms et al. (1987) reported that no concentration effects were found in their experiments. However, concentration effects are in accordance with the theory that the radicals formed during the auto-catalytic oxidation involve reactions with products from the parent compound, in this case quinoline. Wet catalysed oxidation of phenol at ambient temperature showed that the higher phenol to catalyst concentration ratio (copper oxide) the shorter will be the induction periods (Sadana and Katzer, 1974). Although no catalyst was added in these quinoline experiments, the marked decrease in induction period with increasing concentration of quinoline is obvious and in accordance with the findings of Sadana and Katzer (1974). It is likely that the reactor wall promotes some reactions, which will be further discussed under "Reaction mechanisms".

Effect of sampling procedure

In order to acquire more data points in the experiment at 260° C and 250 mg/litre quinoline, an experiment was carried out in which samples were taken every 5 min. This resulted in a prolonged initiation period, as seen in Fig. 4, and thereby a more delayed reaction. The autoclave used in these experiments did not allow sampling during the experiments (meaning at high temperature and pressure). The heating and cooling periods are very short



Fig. 4. Influence of sampling procedure. Initial concentration of quinoline was 250 mg/litre quinoline. Samples were taken after 5 min (\bigcirc) or 10 min (\square) out of the same charge; alternatively, the autoclave was refilled after each reaction period (Δ).

and were previously not found to influence the course of the reaction (Bjerre et al., 1995). On the contrary, it was believed that the heating and cooling periods, although short, facilitated decomposition of the tested compound. In these experiments the opposite situation seems to exist. Therefore, in order to eliminate any influence from heating and cooling periods the autoclave was filled with a new charge of 250 mg/litre quinoline solution after each sampling (Fig. 4). It is seen that the induction period is clearly shorter, although the S-formed curved is still pictured with a similar slope of the rapid reaction phase. However, the sampling procedure could not alone explain the prolonged induction periods seen at the lower temperatures. As mentioned earlier, induction periods have also been observed by others even when sampling took place at elevated temperature and pressure (e.g. Willms et al., 1985). Effects from quenching the reaction have not previously been reported for wet oxidation reactions. Still, these observations were found to be interesting because they clearly show that the oxidation was controlled by some short-lived intermediates, which were obviously "killed" under the cooling process. On the other hand, something was initiated even in the "5-min experiment", or otherwise the reaction would not have started. It is also clear that the concentration of quinoline was slightly decreased under the induction phase, which may indicate that some part of quinoline was transformed to a more activated form. This was directly visible as the samples turned more and more to light purple/red during the experiment. This colour was visible in any experiment just before the fast reaction period and it disappeared after the rapid reaction phase.

Effects of pH

When using no pH-regulating agents, the initial pH was approximately 7. However, it was observed that pH dropped to 4.5 just before the rapid reaction phase started, hence H^+ was generated during the induction periods. In order to investigate the



Fig. 5. Test of pseudo first-order reactions at 260°C. Wet oxidation of 250 mg/litre quinoline at (Δ) acidic,(∇) neutral and (□) alkaline conditions. Wet oxidation of 100 mg/ litre quinoline at (○) neutral conditions.

effect of pH, three experiments were compared, one at high initial pH (>11), one at neutral pH (=7) and one at low pH (=2) using 250 mg/litre quinoline; in all experiments, the reaction conditions were 260°C and a partial oxygen pressure of 20 bar. Samples were taken out of the same bath every 10 min from a cooled reactor; this sampling procedure was found sufficient for illustrating the dependency of pH. In Fig. 5, a plot of $\ln C_a/C_{ao}$ (quinoline concentration/initial quinoline concentration, mg/litre) versus time is shown to test pseudo first-order reactions. The slopes of the lines are estimates of the rate constants for the three experiments (Table 2). The alkaline and acidic experiment fitted very well a first-order reaction compared to that at pH 7, which suffers from lack of sufficient data points. However, making the same test for 100 mg/litre quinoline at pH 7 (same reaction conditions) the reaction seemed to fit a firstorder reaction much better (Fig. 4 and Table 2); the rate constant of this experiment was only 45% of that for the experiment at 250 mg/litre, illustrating the concentration effect. Even though the rate constants are given with some uncertainty, the pH effects are clearly expressed. The acidic reaction was about 2-4 times faster than the neutral reaction, depending on the initial concentration and about 35 times faster than the alkaline reaction. Thus, the reaction rates were very dependent on the initial pH conditions. It is generally considered that reactions of toxic compounds are promoted in an acidic environment (Perkow et al., 1981). In strong alkaline solution. OH-radicals are rapidly converted to the conjugated base O^{•-} (Buxton et al., 1988), leading

Table 2. Rate constants for wet oxidation of quinoline

Temperature (°C)	Initial concentration (mg/litre)	pH conditions	Rate constant, k' (min ⁻¹)	r
260	250	Neutral	0.23	0.92
260	100	Neutral	0.104	0.96
260	250	Acidic	0.4	0.99
260	250	Alkaline	0.011	0.99

to a loss of the strong **•OH** oxidant.

$$^{\bullet}OH + OH^{-} \leftrightarrow O^{\bullet-} + H_2O \tag{1}$$

$$(pK_a(^{\bullet}OH) = 11.7)$$

Reaction products

The strategy of the analytical methods is explained in greater detail elsewhere (Thomsen et al., 1997), but will be presented here briefly. The products identified from an experiment using 100 mg/litre D7-quinoline, a 30-min sample, 260°C and partial oxygen pressure of 20 bar are listed in Table 3. The two samples taken at 10 and 20 min did not show significant amounts of reaction products. Six products including quinoline could be identified by GC/MS and quantified by addition of non-deuterated labelled compounds following workup and a GC/MS run (Fig. 6). The use of non-deuterated labelled compound as internal standards made the analyses straight forward and highly accurate. Besides, by using D₇-labelled quinoline in the wet oxidation experiment, irrelevant peaks in the GC/MS chromatogram could be omitted due to the lack of deuterium in the molecules.

Zwitter-ionic nicotinic acid was found only by silvlation followed by GC/MS detection and quantitatively determined by addition of non-deuterated labelled nicotinic acid, as mentioned above. The corresponding HPLC analysis showed an identical amount, verifying the reliability of the GC/MS method (Thomsen et al., 1997). It is obvious that the main product was nicotinic acid. The formation of nicotinic acid from the four kinetic experiments using 250 mg/litre quinoline in Fig. 2 was measured by HPLC (Fig. 7). It is seen that nicotinic acid is mainly formed after 20 min at temperatures above 220°C, following the TOC curves. It is also seen that nicotinic acid is stable at 240 and 260°C, whereas some degradation could be observed at 280°C. Nicotinic acid was also formed in the experiments carried out at pH 2 and 11, although it formed preferentially at low pH. Thus, nicotinic acid accumulates to some extent during wet oxidation.

Minute amounts of 2-hydroxy-nicotinic acid were found after methylation followed by GC/MS and quantified by HPLC (1–3 ppm at initial concentration of 250 mg/litre quinoline; at 100 mg/litre quinoline, only trace amounts were found). 2-Hydroxy-quinoline was found only by HPLC in the same amount but not in the samples from the acidic treatment. By silylation, succinic acid was unexpectedly found too; succinic acid was quantified by IC together with acetic, formic, glycolic and oxalic acid. Carboxylic acids are common products in wet oxidation (Baillod *et al.*, 1980, Bjerre and Sørensen, 1994). However, the formation of succinic acid can not easily be explained from the decomposition of quinoline itself, but it may be formed by the coup-



Fig. 6. GC/MS-chromatogram of intermediates; 100 mg/litre quinoline, 260°C and 30 min reaction time.

ling of acetic acid radicals (see under "Reaction mechanisms"). No ammonium (NH_4^+) but a small amount of NO_2^- and NO_3^- could be detected.

Mass balance

The experiment with 100 mg/litre D₇-quinoline was used for determining the mass balance. The results of a thoroughly analysed sample is seen in Table 3. For every identified compound a TOC-factor was calculated, being the amount of carbon per mg of the compound in question $(n \times 12/M_w)$, where M_w is molecular weight, g/mol). By multiplying the TOC-factor with the measured concentration (mg/ litre) of the compound in question, the TOC contribution could be calculated as in the following example:



Fig. 7. Production of nicotinic acid from wet oxidation of 250 mg/litre quinoline as a function of time and temperature. TOC contribution from 3-pyridine aldehyde = $C \times \text{TOC-factor} =$ 12.4 mg/litre ×; 0.672 mg-C/mg-aldehyde pyridine =

8.33 mg-TOC/litre

where C is the concentration of a given compound. After 30 min treatment, the measured total TOC content was 59 mg/litre out of 83.7 mg/litre (=100 mg/litre quinoline) corresponding to a CO₂ production of 30%. When comparing this to the TOC measurements in the experiments using 250 mg/litre, this percentage is indeed higher (50%), which verifies the concentration effects. By summarizing all calculated TOC contributions and comparing the result with the measured TOC number for this specific experiment, the mass balance could be determined. It appeared that the identified compounds could account for 70.2% of the measured TOC. This means that 29.8% of quinoline had been transformed into compounds that were not detected by the analysis described in this paper, e.g. polymerized species as suggested for phenol oxidation (Ding et al., 1995).

Reaction mechanisms

The results indicate an auto-catalysed, radical chain reaction presumably involving OH radicals as suggested by others (Sadana and Katzer, 1974; Willms *et al.*, 1987; Joglekar *et al.*, 1991).

The mechanism involved in such reactions are generally described by the following scheme (Hutzinger, 1980):

		Table 3. Products ide	intified by GC/MS, HPLC	and IC including TOC	factors		
Compounds identified	Chemical structure	Molecular weight (g/mol)	Analysis method	Concentration (mg/litre)	Concentration (µM)	TOC factor (mg - C/mg-component)	TOC contribution (mg/litre)
Initial quinoline		129.16	GC/MS	100	774.2	0.837	83.7
Quinoline	8	129.16	GC/MS	1.2	9.2	0.837	1.00
2-Pyridine aldehyde	A CHO	107.11	GC/MS	5.32	49.7	0.672	3.58
3-Pyridine aldehyde	ene care	107.11	GC/MS	12.4	115.7	0.672	8.33
2-Acetyl pyridine	Cocre,	121.14	GC/MS	1.3	10.7	0.693	0.00
3-Acetyl pyridine	CocHs	121.14	GC/MS	5.7	47.1	0.693	3.95
Furo[3,4-b]pyridine-5(2H)on	Ĩ	135.10	GC/MS	0.6	4.4	0.622	0.37
7-Methyl-furo[3,4-b]-pyridine-5(2H)on	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	149.10	GC/MS	0.2	1.3	0.644	0.13
Nicotinic acid	Сооон	123.11	GC/MS,HPLC	27	204.4	0.488	13.17
2-Hydroxy nicotinic acid	но но	139.11	GC/MS	trace	ł	0.518	I
2-Hydroxyquinoline	No.	145.16	НРСС	trace	I	0.744	I
Oxalic acid Succinic acid Glycolic acid Acetic acid Acetic acid Nitrite/Nitrate TOC, measured <i>Σ</i> TOC, calculated	H00C-C00H H00C-(CH.)-C00H CH_0H-C00H CH_0OH HC00H NO5/NO5	90.04 118.09 76.05 60.03 46/62	IC,	2.8 6.1 8.0 1.1 0.2/0.5	31.1 51.7 105.2 183.2 8.7 4.3/8.1	0.191 0.407 0.316 0.316 0.261	0.5 2.53 4.4 0.10 4.1.4 59

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Wet oxidation of quinoline

Initiation	Initiator $\rightarrow 2OH^{\bullet}$	(2)
	$OH^{\bullet} + RH \rightarrow H_2O + R^{\bullet}$	(3)
	$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet}$	(4)
Propagation	$RO_2^{\bullet} + RH \rightarrow RO_2H + R^{\bullet}$	(5)
	$\tilde{2}RO_{2}^{\bullet} \rightarrow 2RO^{\bullet} + O_{2}$	(6)
	$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$	(7)
Termination	$2RO^{\bullet} \rightarrow Products$	(8)

The H-abstraction in reaction (3) is in accordance with findings in gas-phase reactions of hydrocarbons, at temperatures above 420K (Lorenz and Zellner, 1983, Perry et al., 1977). H-abstraction was also postulated to be involved in the wet oxidation of acetamide and acetic acid, where OH radicals were considered to be the dominant oxidising species (Lee, 1990). Since the organic hydroperoxides formed are relatively unstable, decomposition of such intermediates often leads to molecular breakdown and formation of intermediates with lower carbon numbers (Li et al., 1991). However, when using oxygen as the only oxidizing agent corresponding to an "uncatalysed" reaction, the major problem that arises is the argumentation of the initiation step in reaction (2). Oxygen is normally considered too unreactive to be the species which actually abstracts hydrogen (March, 1977). Little is known about the state for the oxygen molecule under pressure in water. The increase in solubility with increasing temperature (Pray et al., 1952) is meant to be due to the decreased hydrogen bonding of water, which permits a higher accommodation of the oxygen molecules into the water (Taylor and Weygandt, 1974). The possibility of a singlet-triplet equilibrium with a hyperactive singlet species was considered, but was rejected due to thermodynamic considerations (Taylor and Weygandt, 1974). A simple explanation of the initial oxidation step is the possible influence of reactor walls. Induction periods are most often explained by the time needed for establishing a stationary concentration of free radicals in solution (Willms et al., 1985). Induction periods have been observed both for the catalysed and uncatalysed oxidition of phenol (Sadana and Katzer 1974; Willms et al., 1985; Joglekar et al., 1991). However, the uncatalysed reaction by Sadana and Katzer (1974), was carried out in a glass-coated reactor and no significant oxidation was found without added catalyst (copper oxide) even at the highest temperature (418 K). In contrast, Willms et al. (1987) demonstrated a significant phenol oxidation at 415 K, in a reactor made of stainless steel. This indicates that the autoclave walls may influence the radical formation, which was also demonstrated for the decomposition of formic acid using two autoclaves made of different construction materials (Bjerre and Sørensen, 1992). In addition, Li et al. (1991) observed that a system which initially contains only oxygen produces hydrogen peroxide, whereas a system which initially contains only H₂O₂ produces oxygen through ther-



Fig. 8. Effect from metal-complex at 220°C: (○) 10 mg/ litre ferroin and 250 mg/litre quinoline; (□) 250 mg/litre without addition of ferroin.

mal decomposition. This implies that the effectiveness of oxygen and hydrogen peroxide as oxidants for wet oxidation of organic compound are kinetically comparable (Li *et al.*, 1991). An example of the production of OH radicals from hydrogen peroxide in the presence of a metal-ion is the wellknown Fenton reaction (9) (Walling, 1975). However, it has been reported that M can be either a homogeneous or heterogeneous species (Hoare *et al.*, 1959).

$$H_2O_2 + M \to 2HO^{\bullet} \tag{9}$$

In the present case the autoclave can contribute with Cu, Mo, Ni or Fe. In the presence of Raney-Ni metal, quinoline is able to make complexes followed by an oxidation/dimerization of coupled quinoline molecules (Badger and Sasse, 1963). The small drop in quinoline and TOC concentration under the induction periods could reflect such a reaction of quinoline with Ni on the surface of the reactor walls. Also the pH-drop and lack of reaction products in the samples taken before the rapid reaction phase can be explained by this hypothesis.

The possible influence of a Ni-complex facilitating hydroxyl radical generation is suggested due to a small amount of Ni (195 μ g/litre) observed in solution in a sample taken just before the rapid reaction phase; in the next sample, where the light purple colour became visible, the Ni content was reduced to 35 μ g/litre. Thus, the induction periods could be explained by the time needed for the generation of such a Ni-complex catalysing the production of OH-radicals either on the reactor wall or in solution. Reaction (2) can then be expressed by a combination of reactions (10a), (10b), (10c) and (9) in accordance with Li *et al.* (1991):

$$H_2O + O_2 + quinoline complex_{(reactor wall)}$$

 $\rightarrow HO_2^{\bullet} + HO^{\bullet}$

$$HO_{2}^{\bullet} + H_{2}O \rightarrow H_{2}O_{2} + OH^{\bullet}$$
(10b)

(10a)

$$\mathrm{HO}^{\bullet} + \mathrm{HO}^{\bullet} \to \mathrm{H}_{2}\mathrm{O}_{2} \tag{10c}$$

The H_2O_2 formed enters reaction 9. The initial rates for subcritical oxygen/water oxidation is expected to be lower compared to that of hydrogen peroxide



Fig. 9. Reaction mechanism of wet oxidation of quinoline, assuming non-charged intermediates.

due to the limited mass transfer between the gas and liquid phases (Li *et al.*, 1991). In order to verify the positive catalytic effect from a relevant metal complex, an experiment was carried out using 250 mg/litre quinoline and 10 mg/litre ferro-*o*-phenantroline (ferroin). The reaction was started without an induction period even at $220^{\circ}C$ as seen in Fig. 8.

The products identified from wet oxidation of quinoline indicates that the initial oxidation mainly occurs at positions 2, 5 and 8. Considering the reaction between quinoline and OH^{\bullet} an addition to the

aromatic ring may take place the same way as for an ordinary electrophile. At higher temperature a direct abstraction of a hydrogen atom becomes increasingly more important (Perry et al., 1977). Difference in localization energy may give rise to some selectivity in the addition process as well as different reactivities of the C-H bonds may cause a more or less specific abstraction of hydrogen. On the other hand, the high process temperatures tend to diminish this selectivity of the reaction. It should be emphasized that the aromatic intermediates identified all retain the pyridine moiety. However, a detailed mass balance shows that the pyridine moiety products accounted for only 59 mol% of the quinoline added (Table 3). Thus, the oxidation of the pyridine moiety may take place on the assumption that this causes an extensive degradation of the molecule leaving no aromatic intermediates.

The only product derived from oxidation at position 2 is 2-hydroxyquinoline, which was found to be very resistant to further treatment at 260°C (data not shown). The reaction mechanism at initial pH 7 involving oxidation at positions 5 and 8 is shown in Fig. 9. It is based on three ring opening processes via quinoline(5,8)dion, quinoline(5,6)dion and quinoline(7,8)dion. These cleavages of the homocyclic (benzene) ring are analogous to that accepted for phenol oxidation (Devlin and Harris, 1984) and are in accordance with the mechanism suggested for the phototransformation of naphthalene adsorbed on, for example, titanium dioxide (Guillard et al., 1993). All ring openings add to the formation of nicotinic acid, whereas only the ring opening via quinoline(5,6)dion leads to the formation of the lactones and 2-acetyl pyridine. Decarboxylation seems to be an important part of the reaction mechanism, which is highly accelerated in acidic environment. Quinolinic acid, the pyridine analogue to phthalic acid, is believed to be an important but unstable intermediate due to decarboxylation. In ozonation, a low temperature, hydroxylradical generating process, quinolinic acid was the main product (Andreozzi et al., 1992).

Acetic acid is produced from oxidation at ring openings 5,6 and 7,8. As no other carboxylic acid derives directly from the ring opening processes, the formation of the oxalic, glycolic and formic acids are suggested to be generated by the further oxidation of acetic acid due to the reactive, hydroxyl radical environment. The formation of succinic acid is difficult to explain from quinoline oxidation. Devlin and Harris (1984) claim that succinic acid is formed by the addition of hydrogen to maleic acid, which was produced under wet oxidation of phenol. First of all, maleic acid was not detected under wet oxidation of quinoline, and, secondly, it seems unlikely that a specific reductive reaction occurred under highly oxidative conditions. A more plausible explanation is the oxidative coupling of acetic acid effected by hydroxyl radical, which was thoroughly

investigated by Coffmann *et al.* (1957). Among many coupling products, succinic acid was produced from acetic acid as the only reactant in the presence of hydroxyl radicals, produced by hydrogen peroxide and ferrous sulphate (Fenton's reagent). To verify this reaction mechanism, an autoclave experiment was carried out using acetic acid, hydrogen peroxide and ferrous sulphate as the only reactants; the results showed a significant production of succinic acid (approx. 6%) after 30 min reaction time. In this experiment, formic, oxalic and glycolic acids were also produced verifying the proposed reaction mechanism for the formation of carboxylic acids as stated above and the involvement of hydroxyl radicals in the reaction mechanism.

CONCLUSIONS

- 1. Quinoline is decomposable by wet oxidation at temperatures of 240°C and above. The reaction is highly accelerated in neutral to acidic environments but markedly slowed down under alkaline conditions.
- 2. The course of reaction indicates that hydroxyl radical mechanisms are responsible for the oxidation depending on the initial concentration of quinoline. The influence of sampling procedure and the production of succinic acid from quinoline confirms the presence of hydroxyl radicals under wet oxidation conditions. The initial production of hydroxyl radicals is suggested to involve elemental Ni or a quinoline-metal complex in solution.
- 3. Nicotinic acid is the main product accounting for up to 35% of the initial quinoline concentration. Acetic acid is produced in an early stage from quinoline oxidation. The production of succinic, oxalic, formic and glycolic acids are all derivatives from the further oxidation of acetic acid.

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