Impact of Common Salts on Oxidation of Alcohols and Chlorinated Hydrocarbons

G. J. Suppes, S. Roy, and J. Ruckman
Dept. of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045

Aqueous oxidations of phenol, methanol, ethanol, n-propanol, n-butanol, chloroethanol, chloropropane and chlorobutane were conducted to evaluate the impact of common salts and bases on oxidation with hydrogen peroxide. Oxidation rates increased up to greater than two orders of magnitude, depending on the electrolytes. Sodium and potassium electrolytes generally promoted oxidation at temperatures near 100°C with sodium promoting oxidation better than potassium. Ionic interactions among electrolytes change the nature of their catalytic activity. In the presence of nitric acid, calcium was the most effective of these metals for promoting oxidation. Using soluble salts is proposed for wet-air oxidation and contaminated soil treatment.

Introduction

Although salts and bases containing sodium, potassium, and calcium are common in wastewater, little data are available on the impact of these constituents on wet-air oxidation, near-critical water oxidation, and supercritical water oxidation rates. An improved understanding of the impact of these salts and bases is important to properly design oxidation processes for wastes containing these constituents. In addition, these salts and bases may provide improved approaches for the efficient destruction of chlorinated hydrocarbons, as well as environmentally-benign catalysts that could be used to improve wet-air, near-critical, and supercritical water oxidation processes.

This article summarizes the wet-air oxidation of several alcohols and chlorinated hydrocarbons using hydrogen peroxide. Designed experiments were used to evaluate the impact of salts and bases on oxidation of the reagents at temperatures between 70 and 120°C. An emphasis was placed on evaluating the catalytic properties of salts and bases commonly found in the environment; specifically, salts and bases containing Na, K, Ca, CO_3, Cl, nitrates, phosphates, and hydroxides.

In addition to being common in waste streams, many of these salts and bases are also common in the environment. Prospective catalysts would have inherent advantages of being environmentally benign, cost-effective, readily available, and easily disposable.

For chlorinated hydrocarbons, several of these electrolytes would also provide a source of metals for neutralizing chlorine to salts. Salt formation is desirable since (1) most of the inorganic salts of chlorine are relatively benign and (2) the low Gibb's free energy of the salts provides a reaction equilibrium favoring the destruction of the chlorinated hydrocarbons.

Background

The advantages of using liquid water as the medium for oxidation are: (1) the high density can lead to smaller and less expensive reactors, (2) higher salt solubilities keep salts in solution, and (3) a relatively constant heat capacity allows for efficient recuperative heating that avoids pinch points associated with large changes in fluid densities.

The primary disadvantages of oxidation in a liquid water phases are: (1) diatomic oxygen has a low solubility; and (2) limiting reaction temperatures to sub-critical regions limits the extent to which temperature can be used to increase reaction rates.

Oxidation rates of model organic wastes in water have been reported by several researchers (Mishra et al., 1995; Savage, 1999; Savage et al., 1995; Thornton and Savage, 1992; Ding et al., 1995; Rice and Steeper, 1998; Tester et al., 1993; Tester and Tester, 1994; Armellini and Tester, 1991); however, little research has been conducted on the impact of salts and bases commonly found in the environment on oxidation destruction.

Correspondence concerning this article should be addressed to G. J. Suppes.

Fierro and Garcia de la Banda (1986) and Novakova (1971) attribute much of the catalytic activity of oxidation to ionic pathways that enhance the heterolytic reactions. Penninger and Kolmschate (1989) and others (Boock et al., 1993; Klein et al., 1992) report hydrolysis in water to follow a polar or heterolytic nucleophilic substitution mechanism. High dielectric constants and electrolytes are reported to stabilize the transitions states for this reaction and lead to increased reaction rates (Torry et al., 1992). This background suggests that the proposed environmentally benign electrolytes of this study will increase destruction rates of the alcohols and cholorinated hydrocarbons.

Torry et al. (1992) are among the few who have investigated the impact of sodium, potassium, or calcium salts reporting a maximum of a 40% increase in reactivity with NaCl toward the hydrolysis of dibenzyl ether. Torry et al. observed a maximum in reactivity as a function of salt concentration that was attributed to formation of brine phase at 380°C.

No previous data were located on the impact of environmentally benign salts and bases as CaO, $CaCO_3$, hydroxides, and nitrates of Na and K, as well as NaCl on HOOH driven oxidation at temperatures $< 250°C$. Several of these salts were observed to be effective at temperatures $> 250°$ (Ross et al., 2000). In soil (temperatures $< 250°C$) quicklime (CaO) and chemical dechlorination have been investigated for destroying PCBs. Quicklime was reported to be ineffective (Amend and Lederman, 1992); however, a successful approach was reported using alkali metal polyethylene glycolate reagents that dechlorinated PCBs in both liquid and soil matrices.

Considerable research has been conducted on supercritical water oxidation, especially on the propensity of salts to precipitate from solution at supercritical conditions. Armellini and Tester (1991, 1993) evaluated the precipitation of NaCl and Na_2SO_4 from supercritical water. These salts created processing problems in supercritical fluids by precipitating onto surfaces. To avoid potential solubility problems, the present investigation was limited to liquid-like densities.

Oxidants commonly used for wet-air oxidation include O_3, ClO_2, Cl_2, HOOH, and O_2 (Mishra et al., 1995). For the present study, hydrogen peroxide was chosen as the oxidant because it is totally miscible at the reaction conditions. Hydrogen peroxide participates in oxidation by forming OH radicals that can attack organic compounds, typically with reaction rates exceeding those attained with diatomic oxygen as the oxidant (Savage, 1999; Brock and Savage, 1995). In practice HOOH can find utility with low organic concentrations (resulting in low consumption of this expensive oxidant) or as a polishing treatment to remove trace amounts of organic components remaining in a waste stream. Dagaut et al. (1996) report that diatomic oxygen oxidizes methanol through HOOH as an intermediate; hence, kinetic data on HOOH driven oxidation have implications on oxidation by other oxidants.

Phenol was chosen for the present investigation, because it is a known refractory compound—a compound difficult to completely oxidize, often being a relatively stable intermediate formed during the oxidation of larger molecules.

Methanol, ethanol, *n*-propanol, and *n*-butanol were also investigated. Their simple structures combined with respective systematic changes in their structures facilitate the extrapolation of results to related molecules and will facilitate in-depth studies of oxidation mechanisms in the presence of these ions (ongoing research). Moreover, all these compounds are representative of industrial waste.

Table 1. Alcohols and Halogenated Hydrocarbons Evaluated

Model Compound	Salts, Bases, and Oxidant
Methanol	HOOH
Ethanol	HNO_3
Propanol	KOH
Butanol	KNO_3
Phenol	NaOH
1-Chloroethanol	$NaNO_3$
1-Chloropropane	NaH_2PO_4
2-Chlorobutane	NaCl
	CaO
	$CaCO_3$

Chloroethanol, chloropropane, and chlorobutane were selected for investigation, because they are structurally similar to the linear of the alcohols and because of the importance of the destruction of chlorinated hydrocarbons. Chlorinated hydrocarbons are among the most toxic of organic compounds, often being incorporated in pesticides. Regulations concerning their destruction are also among the strictest with the Toxic Substances Control Act (TACA) of 1976 requiring six nines (99.9999%) destruction of polychlorinated biphenyl (PCB) compounds. During incineration, new chlorinated compounds including dioxins and furans can be formed if the temperatures and conditions do not properly neutralize the chlorine reactivity (Kimbrough and Wakakuwa, 1992).

Experimental Work

A series of designed experiments were performed in liquid water as a screening process to identify reactions, conditions, and ionic catalysts for subsequent investigation at higher temperatures and pressures. Batch reactions were performed in liquid water to evaluate the impact of electrolytes commonly found in the environment on the HOOH driven oxidation of several alcohols and chlorinated hydrocarbons. Table 1 summarizes the model compounds that underwent oxidation and the bases, salts, and oxidants used to promote oxidation.

Designed experiments simultaneously evaluated several factors impacting reaction half-lives. As experience was gained on the factors and their interaction, the designed experiments were modified to provide greater insight. Three of the Plackett-Burman (PB) designs are summarized in Tables 2 and 3. Chronologically, phenol was the first system to be investigated (design 1), then methanol (design 2), and finally ethanol, *n*-propanol, and *n*-butanol (design 3).

Detailed mathematics behind the PB design of experimentation are given elsewhere (Wheeler, 1998, 1989). These methods are based on ANalysis Of VAriance, commonly abbreviated ANOVA. The experiments of this study were designed to identify how factors result in variance of reaction half-lives from a base case. The PB design allows multiple factors to be simultaneously evaluated with results reported in minutes change in half-lives.

For phenol oxidation, eleven different experimental factors were selected (Table 2, design 1). Two different levels of each factor were used to arrive at twelve experiments constituting the design. In Table 2, the higher level of each factor is indicated in the design by a "plus sign" and the lower level is indicated by a "minus sign."

Prior to performing the designed experiments, preliminary runs were performed to confirm that conversions between 30% and 99% would be observed within the 15 min to 24-h sample times of the designed experiments. Reaction temperatures of 70°C to 90°C achieved these conversions with phenol. Of the electrolytes evaluated, only CaO and CaO_3 were present as solids.

Reagent concentrations were followed as a function of time. Assuming an apparent rate model of the form shown by Eq. 1, the reaction orders, n, and rate constants k were calculated by a least-squares method. Half-lives were then calculated using the least-squares values of k and n

$$dC_A/dt = -kC_A^n \tag{1}$$

Experiments were conducted in batch mode in a constant temperature oven. Two mL glass vials with plastic caps and Teflon septum were used as batch reactors at temperatures below 100°C, while 1 mL (approx.) metallic vials (SWEGLOK fittings) were used at temperatures above 100°C. All samples were prepared in a 100 mL round bottom flask. The flasks were cleaned with distilled water and acetone and heated above 200°C for 3 h prior to making reaction mixtures. Prior to use, metallic vials were boiled in water for 1 h, then cleaned in distilled water and acetone, and heated for 3 h above 200°C.

Table 2. Design Parameters and Set Points of Experiments

Factors	Low Level (−)	Mid Level (0)	High Level (+)
Design 1: used with phenol			
Stoichiometry of H_2O_2	1X		2X
Stoichiometry of HNO_3	1X		2X
Temperature (°C)	70		90
Phenol Conc. (ppm)	300		500
KOH	0.00%		0.20%
KNO_3	0.00%		0.20%
CaO	0.00%		0.20%
H_2NaO_4P-H_2O	0.00%		0.20%
$NaNO_3$	0.00%		0.20%
$CaCO_3$	0.00%		0.20%
NaOH	0.00%		0.20%
Design 2: used with methanol			
KOH	0.10%		0.40%
NaOH	0.10%	0.20%	0.40%
CaO	0.10%	0.20%	0.40%
$NaNO_3$	0.10%	0.20%	0.40%
KNO_3	0.10%	0.20%	0.40%
Stoichiometry of H_2O_2	1X	2X	4X
Stoichiometry of HNO_3	1X	2X	4X
Temperature (°C)	80	90	120
Design 3: used with ethanol, propanol, and butanol			
NaOH	0.00%		0.20%
CaO	0.00%		0.20%
$CaCO_3$	0.00%		0.20%
KNO_3	0.00%		0.20%
KOH	0.00%		0.20%
NaCl	0.00%		0.20%
H_2O_2	1X		2X

Table 3. Plackett-Burman (PB) Experimental Designs and Conventional Design Used During Oxidation Studies*

Run	A	B	C	D	E	F	G	H	I	J	K	Response (min)
Basic 12-run Plackett-Burman design matrix used with phenol												
1	−	−	−	−	−	−	−	−	−	−	−	4,781
2	−	−	−	+	+	+	−	−	+	+	+	1,333
3	−	−	+	−	+	+	+	+	−	−	+	2,717
4	−	+	+	−	+	−	−	+	+	+	−	2,107
5	−	+	+	+	−	−	+	−	+	−	+	151
6	−	+	−	+	−	+	+	+	−	+	−	400
7	+	+	−	+	+	−	−	+	−	−	+	2,400
8	+	+	−	−	+	+	+	−	+	−	−	400
9	+	+	+	−	−	+	−	−	−	+	+	182
10	+	−	+	+	−	+	−	+	+	−	−	3,000
11	+	−	+	+	+	−	+	−	−	+	−	19
12	+	−	−	−	−	−	+	+	+	+	+	53

Run	A	B	C	D	E	F	G	Response (min) Ethanol	Response (min) Propanol	Response (min) Butanol
Basic 8 run Plackett-Burman design matrix used with ethanol, propanol, and butanol										
1	−	−	−	−	−	−	−	1,930	1,097	373
2	−	−	−	+	+	+	+	2,872	1,140	352
3	−	+	+	+	+	−	−	2,022	741	308
4	−	+	+	−	−	+	+	6,799	1,789	471
5	+	+	−	−	+	+	−	1,810	458	172
6	+	+	−	+	−	−	+	1,674	596	235
7	+	−	+	+	−	+	−	2,087	1,116	258
8	+	−	+	−	+	−	+	1,660	770	226

Runs	A	B	C	D	E	F	G	H	Respone (min)
Conventional 18-run experimental design used with methanol									
1	−	−	−	−	−	−	−	−	866
2	−	−	0	0	0	0	0	0	147
3	−	−	+	+	+	+	+	+	115
4	−	0	+	0	+	0	−	−	147
5	−	0	0	−	0	−	+	+	5.9
6	−	0	−	+	−	+	0	0	144
7	−	−	−	+	0	0	+	−	111
8	−	+	0	−	+	−	−	0	99
9	−	+	+	0	−	+	0	+	1.7
10	+	+	+	+	0	−	−	0	52
11	+	+	0	0	−	+	+	−	315
12	+	+	−	−	+	0	0	+	0.9
13	+	0	−	0	+	−	+	0	6931
14	+	0	0	+	−	0	−	+	8.8
15	+	0	+	−	0	+	0	−	161
16	+	−	+	−	−	0	+	0	210
17	+	−	0	+	+	−	0	−	770
18	+	−	−	0	0	+	−	+	2.2

*Responses are in min.

The repeatability of the half-lives determined by the indicated least-squares method generally resulted in < 15% deviation in the values of the half-lives. Data reported as conversions at a specified time have < 25% deviation. Conclusions reported later in this article are typically based on changes in half-lives > 30% of the base case.

Standard solutions at 0.1 g/mL were prepared for each inorganic compound being evaluated except for CaO and $CaCO_3$, which are insoluble in water. Standards were also made (50,000 ppm) for the model organic compounds, which were further diluted to get the desirable initial concentration. For each run, a reaction mixture was prepared in a 100 mL flask consisting of 1,000 ppm of a model compound along with the desired amount of each factor according to the reaction matrix (except for design 1, where initial phenol concentration was a factor varied during the experiment). The reaction mixture was transferred to 12 vials that acted as individual batch reactors when placed in the oven.

To obtain concentration profiles, two samples were collected at 1, 2, 4, 7 and 20 h time intervals, quenched in ice water, filtered, and analyzed for alcohol composition. A variety of analytical methods were used for sample analysis including gas chromatography (GC, HP 6890), high-pressure liquid chromatography (HPLC, HP1100), GC-mass spectroscopy, and total carbon analyzer (TOC, Dorman Carbon Analyzer).

Methanol, ethanol, n-butanol, n-propanol, chloroethanol, chloropropane, chlorobutane and a limited number of phenol samples were analyzed by direct aqueous injection using a Hewlett-Packard (HP) 6890 GC equipped with a HP 7683 injector and a flame ionization detector. A Restek stabilwax-DA (30 m, 0.53 mm ID, 1.0 μm film thickness) column was used for the analysis. Standard curves of at least four points were used for linearity with mid-range standards analyzed periodically. Percent deviations of the repeated standards were $< 5\%$. Injection amounts were 1 μL for phenol and 2 μL for the other compounds. The split/splitless injection chamber was set at a 2.5 split and 210°C for phenol and 160°C for the other compounds. Oven temperatures for phenol were initially at 80°C for 1 min, then ramped at 15°C/min to a 160°C hold for 2 min, and then ramped at 30°C/min to a 210°C hold for 4 min. Oven temperatures for methanol, ethanol, *n*-butanol, and *n*-propanol were initially 40°C for 1 min, and then ramped at 20°C/min to 180°C. With the helium carrier gas flowing at 5.4 mL/min, typical retention times were 3.57, 3.83, 4.46, 4.58, and 11.58 for methanol, ethanol, n-butanol, n-propanol, and phenol, respectively.

Samples evaluated in both the GC and HPLC were analyzed directly as aqueous samples without removal of soluble ions.

Phenol compositions were analyzed primarily in a Hewlett-Packard 1100 series isocratic HPLC. A mobile phase made up of 40:60 ratio of acetonitrile-water at a flow rate of 1.0 mL/min and a Syncropak RPP column (250×4.6 mm ID) from Micra Scientific Inc. were used for this purpose. The wavelength of the variable wavelength detector was kept at 254 nm. The typical residence time for phenol was 3.2 min. Concentrations down to 5 ppm with a maximum standard deviation of 2% were detectable.

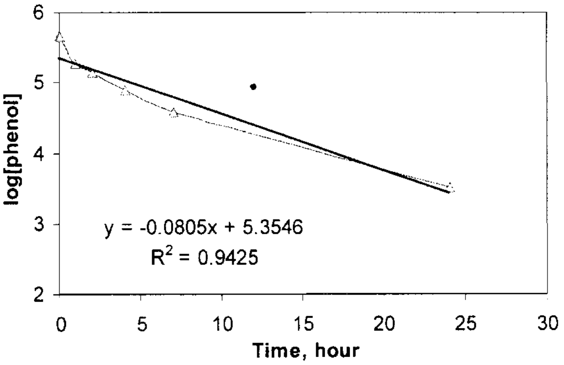

Figure 1. First-order plot for phenol oxidation data.

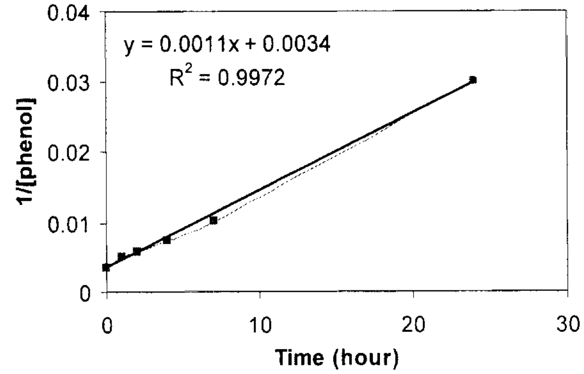

Figure 2. Second-order plot for phenol oxidation data.

The TOC was analyzed using a Dormann Carbon Analyzer for a material balance purpose. The sample was first acidified to pH 4 using *o*-phosphoric acid to drive out any inorganic carbon. The samples were then refrigerated and purged with nitrogen before carrying out TOC analysis. The catalyst for this purpose was prepared by dissolving 60 gm of $K_2S_2O_8$ and 4 mL of H_3PO_4 in 2 L of distilled water. An IR-I detector detected the reacted CO_2 from the analyzer.

All reagents were purchased from Aldrich. Loose crystals of phenol with 99.99% purity were used. Other reagents were HPLC grade with 99.5%+ purity. The inorganic compounds were purchased from Lancaster and Fischer Scientific at $> 99\%$ purity. HOOH (29%) from Fischer Scientific with a maximum impurity of 0.01% sulfate was used as oxidant along with 69.7% HNO_3 (for phenol) with an impurity of < 0.4 ppm. All samples, reagent mixtures, and standards were stored in a refrigerator at 4°C when not in use.

Results and Discussion

Figures 1 and 2 show example concentration vs. time plots used to model the Eq. 1 rate expression. The first-order fit for the phenol data is not good with an R^2 value of 0.943. The second-order plot provided an R^2 value of 0.997. The good fit of the second-order model can be attributed to the fact that near-stoichiometric HOOH was used. For phenol, half-lives were calculated with second-order rate constants evaluated by a least-squares method. For the other reagents, first-order models provided better correlations.

To a large extent, the calculated half-life was independent of the optimal reaction order as long as the model provided a reasonable fit. Using reaction half-lives for comparing reactivities created a common basis for comparison that avoided confusion related to the units of rate constants.

Table 3 summarizes the 12-run, 8-run and 18-run experimental designs used to evaluate the oxidation of phenol, methanol, ethanol, n-propanol, and n-butanol. The wide ranges in half-lives (responses) indicate that the experimental factors had a significant impact on the chemical reactivities of the alcohols. For phenol, reaction rates increased by greater than two orders of magnitude. For designs with HOOH and temperature held constant, the change in reaction rates due to electrolytes was also greater than two orders of magnitude.

Figures 3a, 3b and 3c summarize the estimated effects (sensitivities as calculated by PB method) of each factor indicating the change of half-lives brought about when the level was changed from higher to lower values with other factors kept constant. A large negative value indicates a decrease in half-life.

Calcium oxide (CaO) has the strongest effect on phenol oxidation as seen by the impact of contrast G of Figure 3a. Additional factors having significant impacts include $CaCO_3$, HNO_3, and HOOH. The monobasic sodium phosphate was the only factor that appeared to reduce reaction rates and increase half-lives.

Since CaO and $CaCO_3$ are not consumed during the oxidation, they were by definition exhibiting catalytic capabilities—catalytic capabilities greater than the other seven salts/bases of the experimental matrix. On the other hand, NaH_2PO_4 has a positive estimated effect indicating that it inhibited the reaction. Estimated effects < 20 min are not strong enough to warrant extended discussions. The varying impact of nitric acid can be attributed to the fact that it indirectly impacts oxidation through its interaction with the bases and basic salts present in the system.

The impact of HOOH can be attributed to known oxidation mechanisms that are typically promoted with increasing oxidant concentrations. Due to the number of salts and bases present, additional data are needed to elucidate the behavior CaO, $CaCO_3$, HNO_3, and NaH_2PO_4.

Based on the contrasts of Figures 3b and 3c, the effectiveness of CaO and $CaCO_3$ toward promoting oxidation was significant only when nitric acid was present. The consistency of the performance during ethanol, n-propanol, and n-butanol oxidation (see Figure 3c) provides indirect experimental verification of the results. Nitric acid dissolved both CaO and $CaCO_3$, bringing the calcium ions into the liquid phase where they can best contact the alcohols. The resulting, soluble, calcium nitrate ($Ca(NO_3)_2$) apparently promotes the oxidation similar to the reported impact of copper nitrate ($Cu(NO_3)_2$) (Tagashira et al., 1976; Imamura et al., 1982). The solubility of $Ca(NO_3)_2$ is high at 121 grams per 100 g of water at 18°C (Weast and Astle, 1981).

A key advantage of the homogeneous calcium catalyst over the homogeneous copper catalyst is that calcium can be readily converted to environmentally benign forms. The nitrate groups would likely be utilized by plants and the calcium would form a carbonate or other benign forms for calcium. With half-lives less than 1 h, the extrapolated half-life at ambient temperatures is quite reasonable (~ 16 h).

To check the validity of the methanol oxidation results, an additional designed experiment was performed on methanol. The results are summarized in Table 4. A side-by-side comparison of the effects of the factors of the two designed experiments for methanol is summarized at the end of Table 4

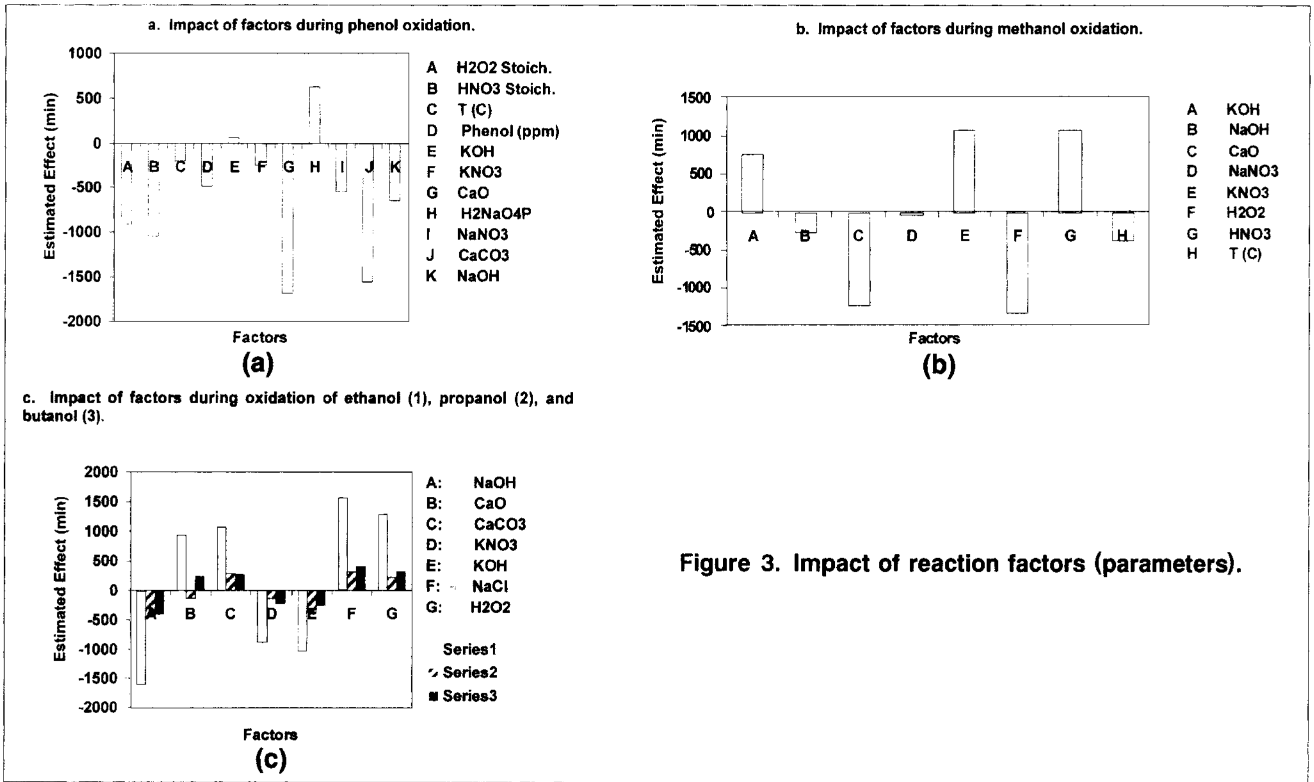

Figure 3. Impact of reaction factors (parameters).

Table 4. Second Methanol PB Designed Experiment

Label	Factor	"−"	"+"
A	KOH	0.0%	0.2%
B	CaO	0.0%	0.2%
C	$CaCO_3$	0.0%	0.2%
D	KNO_3	0.0%	0.2%
E	HOOH	0	2X
F	HNO_3	0	2X
G	T in °C	80	90

Run No.	A	B	C	D	E	F	G	Response (min)
1	−	−	−	−	−	−	−	1,730
2	−	−	−	+	+	+	+	410
3	−	+	+	+	+	−	−	> 5,000
4	−	+	+	−	−	+	+	240
5	+	+	−	−	+	+	−	770
6	+	+	−	+	−	−	+	2,310
7	+	−	+	+	−	+	−	3,470
8	+	−	+	−	+	−	+	> 5,000

Contrast Label	Factor	Effect (min) 2nd	Effect (min) 1st
A	KOH	1,043	760
B	CaO	−573	−1,230
C	$CaCO_3$	−378	
D	KNO_3	863	1,090
E	HOOH	−1,643	−1,330
F	HNO_3	213	1,086
G	T in°C	−753	−373

and shows a total qualitative agreement on the impacts of the common factors between the two designed experiments for methanol. Differences in the values of the effects between the two experiments can be attributed primarily to different contrasts in the concentrations of the salts and bases between the two experiments.

The inhibiting impact of NaH_2PO_4 can be attributed to a buffering effect that may have neutralized the effectiveness of other bases and salts toward promoting oxidation. This was determined to be one of the less interesting of the observed phenomena and was not pursued further.

In addition to the sited impacts of calcium, HOOH, and nitric acid, the methanol oxidation results indicate that sodium compounds tend to promote oxidation better than potassium compounds.

Although consistent and explainable trends were observed with the PB designed experiments, interactions among salts and bases created uncertainty on interpretations. Additional experiments designed to address issues related to interactions were conducted and are summarized in Tables 5 and 6.

Rates of reagent disappearance in the presence of single salts and bases indicate that NaCl effectively and consistently increases reaction rates. This is in contrast to the designed experimental results for ethanol, n-propanol, and n-butanol where NaCl reduced reagent reaction rates.

The data of Table 6 confirm that CaO and $CaCO_3$ do not effectively promote oxidation of methanol and phenol in the absence of nitric acid (at temperatures < 120°C). In addition, the data of Tables 5 and 6 show consistent control experiment results—controls both with and without oxidant present. Optimal reaction orders remain constant at values between 1.4 and 1.7. TOC analyses reveal substantially incomplete oxidation at these low temperatures.

Table 5. Gas Chromatography vs. TOC* Analysis for Phenol Conversion in Batch Reactor at Low Conversions

Salt /Base	Alcohol	TOC**	Intermediates
Phenol concentration (1,000 *ppm*)			
None	751	836	85
NaOH	302	834	532
NaCl	228	714	486
$NaNO_3$	278	800	522
Ethanol concentration (1,000 *ppm*)			
None	957	953	< 50
NaOH	738	912	174
NaCl	394	574	180
$NaNO_3$	856	856	< 50
Propanol concentration (400 *ppm*)			
None	393		—
NaOH	292		—
NaCl	218		—
$NaNO_3$	359		—

*Phenol-Oxidation at 1X HOOH, 80°C, and 120 min.

**TOC adjusted to match alcohol calibration.

The reactivity of the alcohols tend to increase with increasing molecular weight. Methanol is the most resistant to oxidation and phenol is the least resistant to oxidation—albeit phenol's disappearance can be in part attributed to dimerization that is not present with the aliphatic alcohols. Substantially reduced reaction rates in the absence of HOOH indicates (Table 6) that the reactions are substantially oxidative.

During the destruction of chlorinated hydrocarbons, the presence of basic forms of sodium, potassium, and calcium provide strong thermodynamic driving forces toward formation of NaCl, KCl, and $CaCl_2$. Table 7 provides the experimental design used to evaluate chloroethanol with similar experimental designs applied to chloropropanol and chlorobutane. An analysis leading to the estimated effects of each of

Table 6. Different Alcohol Oxidation in Liquid Phase (80°C and 1 barg) with Individual Catalyst*

Sample Description	Half-Lives (h) Methanol	Ethanol	Propanol	Butanol	Phenol
Half lives					
No HOOH	> 120	> 120	> 120	> 120	> 120
1X HOOH	46.4	> 120	8.8	31.9	2.3
1X HOOH and NaOH	25.4	3.7	3.8	0.8	0.6
1X HOOH and $CaCO_3$	29.9	> 48	> 120	18.5	1.7
1X HOOH and CaO	> 120	24.1	> 120	> 48	2.9
1X HOOH and NaCl	22.9	2.3	2.5	0.9	0.6
1X HOOH and $NaNO_3$	25.1	1.4	5.9	2.2	0.8
Reaction order					
1X HOOH	1.6	—	1.6	1.7	1.5
1X HOOH and NaOH	1.6	1.5	1.6	1.6	1.4
1X HOOH and $CaCO_3$	1.7	1.7	—	1.7	1.5
1X HOOH and CaO	—	1.6	—	1.8	1.5
1X HOOH and NaCl	1.7	1.4	1.4	1.4	1.4
1X HOOH and $NaNO_3$	1.6	1.4	1.5	1.6	1.4

*Observed reaction orders varied from 1.4 to 1.7.

Table 7. PB Designed Experiment for Chloroethanol

Label	Factor	"−"	"+"
A	NaOH	0.0%	0.2%
B	CaO	0.0%	0.2%
C	$CaCO_3$	0.0%	0.2%
D	KNO_3	0.0%	0.2%
E	HOOH	0	2X
F	HNO_3	0	2X
G	T in °C	70	90

Run No.	A	B	C	D	E	F	G	Response (min)
1	−	−	−	−	−	−	−	> 5,000
2	−	−	−	+	+	+	+	> 5,000
3	−	+	+	+	+	−	−	~ 50
4	−	+	+	−	−	+	+	> 5,000
5	+	+	−	−	+	+	−	~ 1,000
6	+	+	−	+	−	−	+	< 2
7	+	−	+	+	−	+	−	> 5,000
8	+	−	+	−	+	−	+	< 2

the factors in Table 7 was not possible due to the large range in reactivities. Within the sampling time frame, half-lives for only two of the eight experiments could be estimated. Of the remaining six reactions, four proceeded too slow and two proceeded too fast to reasonably estimate half-lives. Similar observations were made for the reaction of 2-chlorobutane.

Figures 4 and 5 provides typical reaction profiles for the chlorinated hydrocarbons. Figure 4 shows a reaction where the half-life could be estimated, but the data have more scatter than is desired. Figure 5 provides the reaction profile for a reaction that proceeded relatively quickly.

The reaction profile of Figure 5 suggests that a fast reaction between the electrolyte and the chlorinated hydrocarbon proceeds quickly until the reactive electrolyte is consumed. Subsequently, oxidation provides the primary mechanism for destruction proceeding at slower rates.

To evaluate this hypothesis, the reactivity of individual bases and salts with chloroethanol were evaluated individually without the presence of HOOH. The results as summarized in Table 8 indicate a fast and complete reaction of the bases of sodium, potassium, and calcium with chloroethanol. The neutral NaCl salt did not have a driving force toward formation of NaCl and hence did not react. The nitrate and carbonate salts did react, but at slower rates.

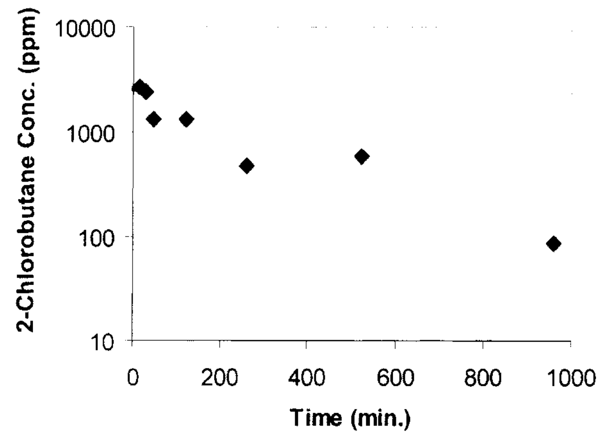

Figure 4. Reaction profile of 2-chlorobutane without salts and bases present.

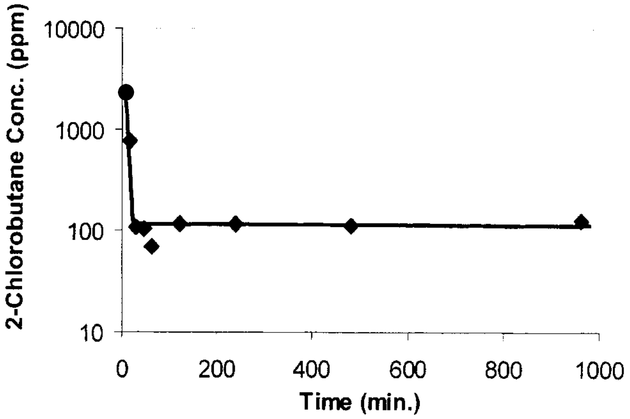

Figure 5. Reaction profile of 2-chlorobutane with bases present.

GC analysis revealed that the predominant organic product was acetaldehyde. The formation of acetaldehyde indicates that chloride salts were also formed.

An effective two-step method for destroying chlorinated hydrocarbons would consist of (1) reacting of the chlorine functionality with a base to form benign salts and (2) subsequent oxidizing of the nonchlorinated intermediates. This approach could potentially be the extent of treatment of contaminated soil. In the case of chloroethanol, the oxidation of the acetaldehyde intermediate is the rate-determining step. Reaction profiles similar to those of Figure 5 were exhibited by all the chlorinated hydrocarbons of this study, indicating that similar two-step approaches would be effective for many chlorinated hydrocarbons.

Metal oxides and hydroperoxides neutralized chlorine substrates most effectively; $CaCO_3$ showed similar reactivity albeit a little slower. Complete oxidation proceeds at considerably slower rates than chlorine neutralization as evident by the acetaldehyde concentrations of Table 8. Calcium carbonate has operational advantages of being inexpensive and neutral in pH. Also, as a solid, a packed bed of $CaCO_3$ would be consumed only to the extent that it reacts.

Table 8. Concentrations for Chloroethanol Reactions (ppm) at 90°C for 1 h*

Factor	Chloroethanol	Acetaldehyde
NaOH	0	1,213
KOH	0	1,340
CaO	0	1,277
KNO_3	975	795
$CaCO_3$	1,120	734
NaCl	2,320	—
None	2,353	—

*Salts and bases are present at about 0.2% without HOOH. GC peaks were prominent during analysis for chloroethanol (10.31 min), acetaldehyde (2.63 min), and an unidentified intermediate (3.29 min).

Deficiencies of the PB designed experiments for evaluating multiple experimental factors include (1) the potential interaction of the factors and (2) the error involved in decoupling the interaction. For example, HNO_3 reacts strongly with the bases, thus depriving these compounds of being used as a catalyst in their original form. Despite these deficiencies, these designed experiments provided valuable insight into the reactions of the study.

Conclusion

Aqueous oxidations of phenol, methanol, ethanol, n-propanol, and n-butanol were typically promoted up to over one-hundred fold by salts and bases. In only a few instances were electrolytes observed to inhibit oxidation. Inhibiting phenomena was attributed to electrolyte-electrolyte interactions rather than electrolyte-hydrocarbon interactions. Sodium chloride strongly promoted oxidation when used in the absence of other electrolytes, but appeared to inhibit reaction when used in combination with calcium-containing electrolytes. Sodium phosphate (NaH_2PO_4) appeared to buffer the impact of other electrolytes and inhibited phenol oxidation. The impact of CaO and $CaCO_3$ was substantially increased when HNO_3 dissolved these solids to form calcium cations in solution. The results of this study imply that $Ca(NO_3)_2$ can serve as a homogeneous catalyst for low-temperature wet-air oxidation processes, similar to, but less toxic and less expensive than, $Cu(NO_3)_2$.

The efficacy of $Ca(NO_3)_2$ was compared to $Cu(NO_3)_2$ by using each of these at 500 ppm with 1,000 ppm phenol with stoichiometric HOOH at 95°C. Conversions were 21% and > 99% respectively with a conversion of 2% for the control. This confirmed the ability of $Ca(NO_3)_2$ to convert phenol. Nitric acid may also promote conversion; however, it was not evaluated further since the contrasts of Table 4 indicate that nitric acid did not promote conversion.

The reactivity of the alcohols toward oxidation increased with increasing molecular weight. At temperatures < 100°C, complete oxidation to carbon dioxide and water was not achieved. Acetaldehyde was the predominant, stable oxygenate intermediate formed from straight-chain alcohols. Phenol dimers were likely formed during phenol oxidation.

Deficiencies of the PB designed experiments for evaluating multiple experimental factors include (1) the potential interaction of the factors and (2) the error involved in decoupling the interaction. For the present studies, experiments evaluating the impact of single electrolytes were needed to provide insight into mechanisms that could not be gained using only the PB designed experiments.

An effective method for destroying at least some classes of chlorinated hydrocarbons involves two steps: (1) the reaction of the chlorine functionality with a base to form benign salts; (2) subsequent oxidation of the nonchlorinated hydrocarbon interemediates. In the case of choloroethanol, the oxidation of the acetaldehyde intermediate is the rate-determining step.

Calcium carbonate exhibited an ability to react with and destroy chlorinated hydrocarbons, while also promoting oxidation of hydrocarbons. These studies indicate that $CaCO_3$ has the potential to provide an increased and valuable role in waste destruction—much greater than current practice.

Acknowledgment

This work was funded by the U.S. EPA, KTEC, and NSF (Grant No. 9810053). Haiming Jin, Mark Rice, Teck Lee, and Jason Fackler performed experiments. Todd Williams of the KU Department of Chemistry provided assistance in setting up the GC and in interpreting the data. Their support is greatly appreciated.

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Manuscript received Aug. 14, 2000, and revision received Jan. 5, 2001.