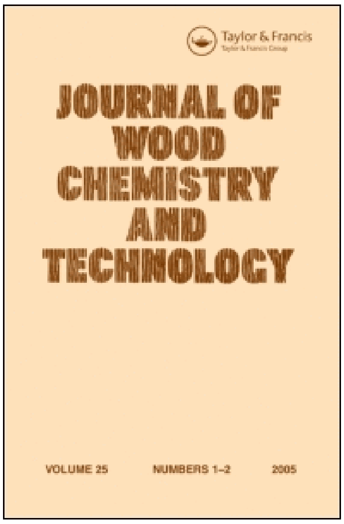

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REACTIONS OF OZONE WITH DIBENZO-*P*-DIOXIN AND DIBENZOFURAN IN PULP

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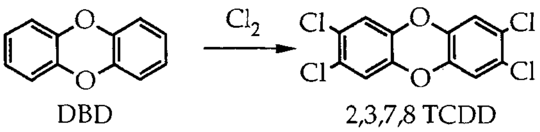
ABSTRACT

Dibenzo-*p*-dioxin (DBD) and dibenzofuran (DBF) appear to be important precursors to chlorinated dioxins formed during chlorine bleaching of pulp. Reducing the concentration of the precursors prior to chlorination may reduce the formation of dioxins. The high reactivity of electrophilic chlorine with the precursors in pulp suggests that ozone, another electrophilic reagent, may effectively reduce precursor levels in pulp. The goal of this work was to find optimal conditions for ozone destruction of DBD and DBF in pulp. Very mild conditions were unsuccessful at removing DBD and DBF, however conditions of 2% ozone charge, high consistency and slow ozone delivery rates reduced DBD and DBF by 83% and 68%, respectively. In general, conditions which enhance delignification also enhanced precursor degradation. Exposure of pulp to ozone prior to chlorination may remove enough DBD and DBF to significantly reduce chlorinated dioxin formation with chlorine bleaching.

INTRODUCTION

The formation of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) during chlorine bleaching of pulp has been the target of extensive research by the pulp and paper industry. Several means of reducing their occurrence have been investigated, including the use of alternative bleaching techniques[1,2] and nonchlorine bleaching reagents.[3,4] Another potential method of minimizing PCDD/F formation is by pretreatment of the pulp to remove PCDD/F precursors prior to chlorination.

Dibenzo-*p*-dioxin (DBD) and dibenzofuran (DBF) are present in pulp.[5] There is evidence that chlorination of these compounds leads to a significant portion of the observed PCDD/F in effluent and pulp.[6] The major PCDD/F congeners that are formed are shown in reactions 1 and 2. Molar yields of approximately 6% 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and 1% 2,3,7,8-tetrachlorodibenzofuran (TCDF) have been reported when DBD- and DBF-spiked pulp was chlorinated; the extent of the disappearance of DBD and DBF was not addressed.[3]



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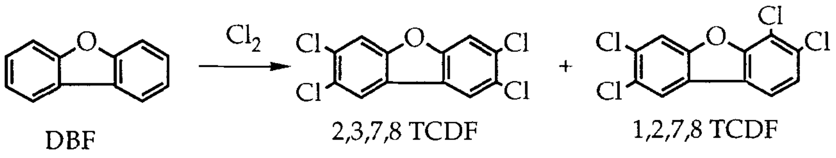

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The chlorination of parts-per-billion levels of DBD and DBF in the presence of percentage levels of lignin suggests that DBD and DBF are highly reactive toward chlorine. It is possible that electrophilic reagents other than chlorine will selectively react with DBD and DBF in the presence of lignin so that subsequent chlorine bleaching will not produce PCDD and PCDF.

In previous work, we examined the reactivities of DBD and DBF toward several compounds, including radical, charged, and neutral electrophiles.[7] Specifically, ozone, nitrogen dioxide, hydrogen peroxide, oxygen under ultraviolet light, and nitric acid were evaluated. The reactions were conducted in solution and in the presence of cotton linters.

Ozone was the most reactive towards DBD and DBF, followed by nitrogen dioxide. Micromolar concentrations of ozone degraded nearly all of the dissolved and adsorbed DBD and DBF while molar concentrations of most of the other reagents were necessary.

Because ozone was so effective at destroying the precursors under conditions where few competing reactions occurred, further study of ozone reactions with precursors adsorbed on pulp was warranted. Pulp contains a large amount of ozone-reactive components, of which lignin is probably the most important. The lignin may consume the ozone before reactions can take place with the precursors. The purpose of this work was to determine if ozone will selectively react with the precursors in the presence of pulp.

RESULTS AND DISCUSSION

Initially, DBD- and DBF-spiked kraft southern pine pulp (27.9 kappa) was ozonated under conditions that were identical to those in earlier work with spiked cotton linters. Batch ozonations were conducted for 15 minutes at 2% consistency, 0.1% ozone charge, and at room temperature.[7] The unbleached pulp contained approximately 4% lignin by weight; therefore, this pulp may compete with the precursors for ozone more successfully than a lower kappa pulp.

There was no degradation of the DBF and about 5% degradation of the DBD upon ozonation of the spiked pulp (Table 1). It is clear that the pulp components effectively compete with the precursors for the ozone, since the same reaction conditions with spiked cotton linters resulted in complete degradation of the precursors. However, it appeared that the DBD was beginning to degrade, even under these extremely mild conditions.

A second set of experiments was conducted in which more stringent reaction conditions were examined. A flow-through reactor

TABLE 1

Reactions of Ozone with DBD and DBF Adsorbed to Pulp

		μmole before O_3	μmole after O_3	% Degraded
Blank				
	DBF	-	ND[a]	-
	DBD	-	< 0.01	-
Experiment 1				
	DBF	1.39	1.41	0
	DBD	1.57	1.49	5
Experiment 2				
	DBF	1.39	1.42	0
	DBD	1.57	1.44	9

[a] ND = Not Detected

allowed a higher ozone charge to be applied to the pulp than was possible in the batch experiments. The same southern pine kraft pulp was used for these experiments. The effects of ozone delivery rate, consistency, ozone charge and temperature on DBD and DBF degradation were evaluated.

A slower delivery rate of ozone resulted in more effective degradation of the precursors (Figure 1). In essence, the slower delivery rate allowed longer reaction times. These results are consistent with an increased consumption of ozone with lower delivery rates,[4] which suggests that longer reaction times allow more extensive reactions to take place, both with lignin and with the precursors.

As expected, increasing the charge of ozone decreased the concentration of DBD and DBF remaining in the pulp (Figure 2). Although there was a fairly linear relationship between O_3 charge and DBD and DBF concentration (r^2 = .99 and .97, respectively), the curve

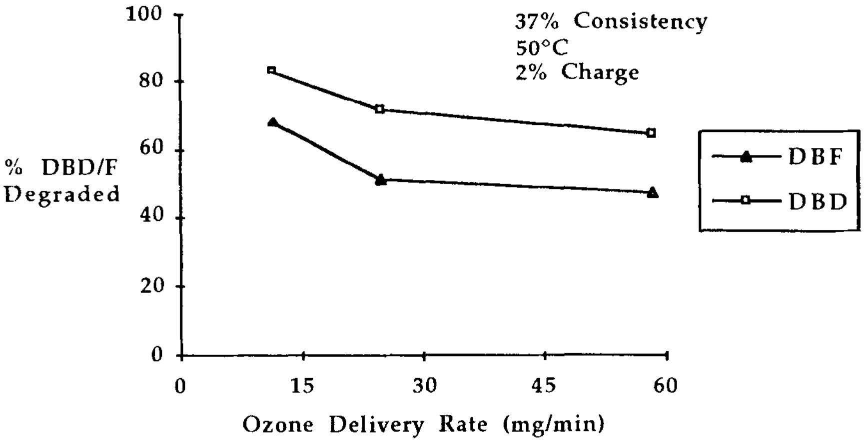

Figure 1. Effect of Ozone Delivery Rate on DBD and DBF Degradation.

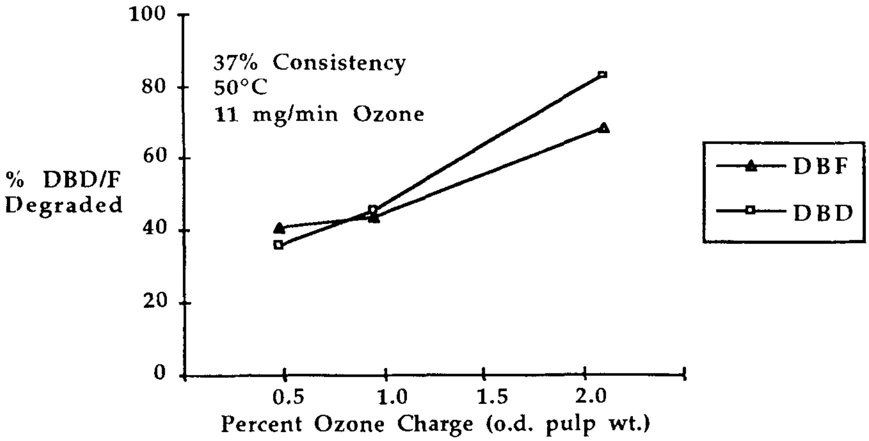

Figure 2. Effect of Ozone Charge on DBD and DBF Degradation on Pulp.

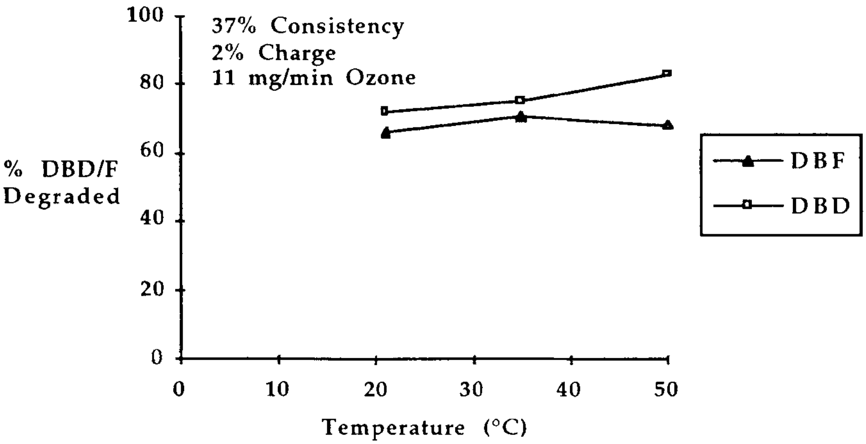

Figure 3. Effect of Temperature on DBD and DBF Degradation on Pulp.

from these very limited data suggest that there may be an O_3 concentration threshold beyond which DBD and DBF reactivities increase. It is reasonable that there would be an increase in precursor degradation when lignin concentration is reduced; such a phenomenon would cause the apparent effect that was observed.

Temperature had a fairly insignificant effect on the precursor degradation (Figure 3). Ozone concentration may be expected to decrease with an increase in temperature due to decomposition[10] and reduced water solubility; even so, medium consistency ozone delignification has little dependence on temperature up to 56°C.[9] Under the high consistency conditions used in this study, the DBD degraded a little more at 50° than at 20°C, while there appeared to be no effect on DBF degradation.

High consistency conditions produced the most precursor degradation (Figure 4). The results of the consistency experiments are likely to be somewhat confounded by the mechanical difficulties associated with adequate mixing at medium consistency with our apparatus. However, the dip in precursor degradation at 12%

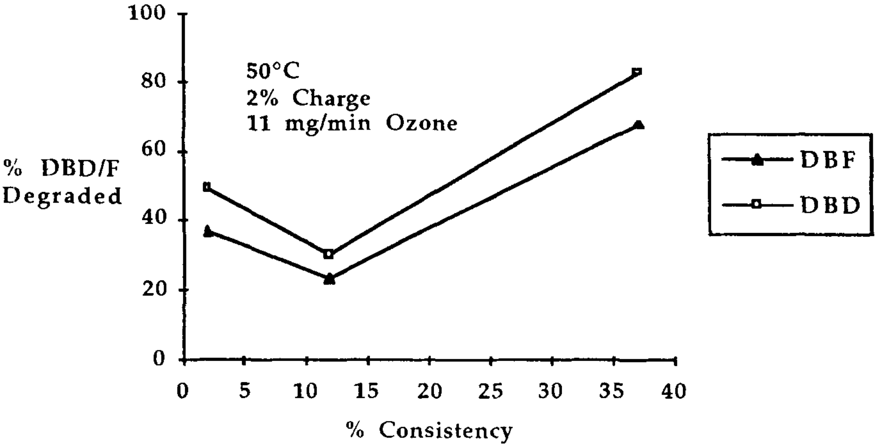

Figure 4. Effect of Consistency on DBD and DBF Degradation on Pulp.

consistency corresponds to a decrease in reactivity to lignin with medium consistency ozonation[8,9] under standard mixing conditions. The diffusion of ozone through the immobile water phase adjacent to the fibers can be a rate limiting step in ozone delignification if effective mixing is not utilized.[8] Delignification and also, presumably, degradation of adsorbed DBD and DBF would be enhanced with a smaller immobile water layer which occurs with higher consistencies and highly effective mixing.

The diffusion of ozone into the cell wall to the lignin is another rate-limiting step in ozone delignification.[8] Thus, the location of the precursors with respect to the cell wall may prove to be an important factor in the relative reactivities of ozone with the precursors and lignin. Furthermore, the source of the DBD and DBF would likely influence their location in or on the fibers, thereby influencing their reactivity to ozone relative to lignin.

There are several mechanisms by which the ozone could destroy the precursors. The ozone may react with the precursors by a 1,3 dipolar addition to an aromatic bond, producing carboxylic acids, aldehydes, and carbon dioxide by way of ozonide and peroxide intermediates.[11-13] Electrophilic addition and substitution reactions which produce hydroxylated aromatics and quinones from oxygen substituted aromatics are other potential reaction pathways.[12-14] In all of these experiments, degradation products were not detected. However, high molecular weight materials (from coupling reactions), CO_2, and highly polar compounds, such as carboxylic acids, would not have been detected with our methods of analysis.

Under most conditions, DBF was less reactive than DBD which is consistent with the work done in solution and on cotton linters.[7] The rates of 1,3 dipolar addition and electrophilic substitution for substituted benzenes increase with electron-donating capacity of the substituents.[11,15] The electrophilic nature of the reaction may be important in understanding the differences between DBD and DBF reactivities and between the precursors and lignin. Hammett σ values reflect the stabilization provided by substituents during electrophilic aromatic substitution reactions. The σ_p and σ_p^+ of an aryl ether (- 0.320 and - 0.5, respectively) are more negative than σ_p and σ_p^+ of a phenyl group (- 0.01 and - 0.179, respectively[16,17]) indicating that an aryl ether has a higher electron donating capacity than a phenyl substituent. Consequently, the DBD, with two aryl ether linkages, should be more reactive than the DBF toward electrophilic attack.

In summary, pulp components successfully competed with the precursors for ozone under extremely mild reaction conditions (e.g., cold reaction temperatures, low ozone charge). However, under conditions in which ozone reactivity was optimized, 68% of the DBF and 83% of the DBD was degraded. In general, conditions which enhance delignification also enhance precursor degradation. High (2%) ozone charge and high consistency promoted precursor degradation. Reaction of the precursors increased somewhat with slower ozone delivery rates; temperature had the least effect. It is likely that pulp with a lower lignin content (e.g., oxygen delignified pulp) will consume less ozone resulting in more precursor degradation. Exposure of pulp to ozone prior to chlorination may remove enough DBD and DBF to significantly reduce TCDD and TCDF formation during chlorine bleaching.

EXPERIMENTAL

The DBD and DBF were applied to the unbleached, oven-dried, southern pine kraft pulp (27.9 kappa) by soaking the pulp in a methylene chloride solution of the precursors. The excess solvent was later evaporated from the pulp. The pulp was acidified to pH 2 with sulfuric acid or acetic acid, filtered to high consistency, and frozen or refrigerated until used. Initial values of 30 ug DBD /o.d. g pulp and 37 ug DBF/o.d. g pulp were determined by analysis of the spiked pulp.

The DBD and DBF in pulp were isolated by soxhlet extracting acetone-wetted pulp using hexane. The pulp was spiked with internal standard, 2-methoxybiphenyl prior to extraction. The extract was concentrated and analyzed by gas chromatography with a flame ionization detector (30 m DB-5 capillary column; 2 mL/min flow rate; 245°C injector; 300°C detector; initial oven temperature 90°C, hold 1 min., 10°C/min. ramp to 295°C). Aqueous samples were extracted in a separatory funnel three times with hexane after being spiked with internal standard. Detection limits were in the parts per billion range.

In the first set of experiments, a control (no ozonation of the acidic solution), a blank (no DBD and DBF) and two experimental samples were evaluated. An O_2/O_3 gas mixture, generated by a Welsbach T 816 ozonator, was bubbled through an acetic acid solution at pH 2 for 45 min. The ozone concentration in the acid water was 525 μM, as determined by iodometric titration. Approximately 10 g of pulp was placed in 500 mL of the ozonated acid water. After 30 minutes, the mixture was filtered and the pulp and filtrate were analyzed.

In the second set of experiments in which the effects of reaction variables were examined, the ozone/oxygen stream was delivered to a modified rotoevaporator which contained 5.5 o.d. g pulp, except for temperature experiments in which 2.7 o.d. g was ozonated. Ozone concentrations were measured by passing the ozone through a potassium iodide trap and titrating the trap solutions with sodium thiosulfate. In this paper, ozone charge is that quantity applied to the pulp on a percent weight basis.

The ozone delivery rate was altered by changing the concentration of ozone in the O_2/O_3. The same charge was maintained by adjusting the time of delivery. The other conditions used were 50°C, 37% consistency and 2% ozone charge (on o.d. pulp). The delivery rates utilized were 11.5 mg/min., 24.8 mg/min., and 58.3 mg/min.

The consistencies examined were 37%, 12% and 2%. An acetic acid solution of pH 2.14 was used to adjust the consistency of the latter two samples. Other reaction conditions included a 12 mg/min. delivery rate, 50°C and 2% charge. The 10% consistency sample was difficult to mix effectively; the pulp stuck to the sides of the flask.

The charge was adjusted by changing the time of delivery at identical delivery rates. The charges examined were 0.5%, 1.0% and 2.1%. Other reaction conditions were 50°C, 11 mg/min. delivery rate and 37% consistency.

The temperatures examined were 50°C, 35°C and 21°C. These were attained by placing the rotating round bottom flask in a water bath at the appropriate temperature. The apparatus was allowed to equilibrate for a few minutes before ozone was introduced. In the high temperature, some vaporization of the water in the pulp occurred. Other reaction conditions were 11 mg/min delivery rate, 2% charge and 37% consistency.

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