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# **Bleaching Kraft Pulps with In-Situ Generated Dioxiranes**

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**ABSTRACT:** The catalytic properties of aliphatic ketones to accelerate bleaching reactions of peroxymonosulfate with kraft softwood pulp was studied. The in-situ generation of substituted dioxiranes from keto-compounds and peroxymonosulfate was demonstrated to be an effective bleaching technology. This bleaching system was shown to be very sensitive to the nature of the alkyl groups attached to the carbonyl group. The use of either very reactive ketones and/or hydrophobic structures was shown to be detrimental to the overall bleaching process.

## **I. Introduction**

Bleaching of kraft pulps is undergoing profound technical changes as environmental and market forces have combined to substantially alter this process (Browner, 1993; Cockram, 1991). Current kraft bleaching operations have considerably improved waste management practices and research efforts are continuing to improve the environmental performance of these operations (Hise, R.G., 1992). To address future needs researchers have examined a variety of oxidative bleaching technologies including molecular oxygen (Tench and Harper, 1987), hydrogen peroxide (Lachapellen et al., 1992), peracids (Hill et al., 1992; Muurinen and Sohlo, 1991) and ozone (Liebergott, 1992). To date, only ozone technology has developed sufficiently so as to allow for commercial applications. Nonetheless, there is generally acknowledged a need to continue exploring alternative bleaching technologies which will complement the bleaching capabilities of ozone.

Recently, several research institutions (Lee et al., 1993a, 1993b; Ragauskas, 1993) have begun to investigate the bleaching capabilities of dimethyldioxirane (DMD). This

cyclic three member peroxide structure, illustrated in Figure 1, has shown much promise as an efficient, selective, bleaching agent for kraft pulps. Based upon numerous fundamental research investigations (Adam, 1989; Murray, 1989), it is well established that dimethyldioxirane is an effective oxidizing agent which can be generated from acetone and peroxymonosulfate (see Fig. 1). The resulting dioxirane can be isolated, or as in the case with kraft pulps, generated and employed in-situ. Upon oxidation of a substrate with DMD, oxygen is transferred to the substrate and acetone is re-generated (see Fig 1). In this manner, acetone acts as a true catalyst and therefore can be employed in relatively small amounts and recovered upon completion of the reaction. Investigative studies by Ragauskas (1993) and Lee et al. (1993) have shown that DMD is a very effective reagent for the delignification of kraft pulps. Preliminary investigative studies demonstrated that a freshly prepared solution of DMD in acetone was very effective at removing lignin from kraft pulps. Employing a 5% charge of a DMD/acetone solution, Ragauskas demonstrated that 66% of the lignin present in a softwood kraft pulp could be removed. This level of delignification had previously only been observed with ozone (Nutt et al., 1993). Studies by Lee and Ragauskas have both demonstrated that these results can also be achieved employing in-situ generated DMD. In-situ generation of DMD is an attractive technology for bleaching kraft pulps since it avoids the need to isolate this reactive peroxide and takes full advantage of the catalytic properties of acetone and peroxymonosulfate.

Although the bleaching properties of DMD hold much promise, many technical challenges need to be resolved prior to full commercial application, including bleaching sequence studies, design of a DMD bleaching reactor, and further improvements in our fundamental knowledge of dioxirane bleaching chemistry. Research efforts by Lee (1992), Qui (1993), and McDonough (1994) have begun to examine bleaching sequence studies with DMD. Studies directed by Lee are examining the technical issues surrounding commercial applications of DMD, including on-site generation of peroxymonosulfate and recovery of acetone. Our own studies have recently focused on the sensitivity of DMD to metals present in kraft pulps and the potential application of alternative dioxirane

structures for bleaching kraft pulps. In this report we wish to describe the results of our studies directed at bleaching kraft pulp from in-situ generated substituted dioxiranes.

## **2. Experimental**

All reagents were commercially purchased and used without further purification. Oxone<sup>TM</sup>, a triple salt of  $K_2SO_4 \bullet KHSO_4 \bullet KHOSO_4$  was employed as a source of peroxymonosulfate. The softwood kraft pulp was prepared from commercial wood chips in a laboratory digester.

All bleaching experiments were executed following standard laboratory conditions for handling peroxides (National Academy Press, 1981). The standard bleaching procedure consisted of adding a softwood kraft pulp (63 g fiber, oven dry weight) and  $NaHCO_3$  to water (2.50 l) and then adding the ketone solvent (2.45 mol) to an open beaker in a well ventilated fume hood. This mixture was then vigorously stirred and the peroxymonosulfate was added over the duration of 10 min. After vigorously stirring this mixture for 1 h the pulp slurry was filtered, washed and analyzed for lignin content, viscosity, and Tappi brightness values following standard testing methods (TAPPI, 1992). The pulp was then extracted with an aqueous 0.04 N solution of NaOH (1000 ml alkaline solution/30 g of fiber). After stirring for 1 h at RT, the mixture was filtered and washed. The resulting pulp was analyzed for lignin content, viscosity, and Tappi brightness values as described above.

## **3. Results and Discussion**

To date, only dimethyldioxirane has been reported to be an effective dioxirane bleaching agent for kraft pulps (Murray and Jeyaraman, 1985). Nonetheless, a variety of dioxirane structures have been prepared and employed for general oxidative chemistry purposes. Indeed, a review of the chemical literature indicates that acetone may be one of the least effective dioxiranes generated from peroxymonosulfate. Early studies by Montgomery (1974) demonstrated that cyclohexanone and N,N-dimethyl-4-oxo-piperidium nitrate were substantially more effective at catalyzing peroxymonosulfate reactions than

acetone. Studies since this paper have shown that trifluoroacetone is another effective ketone precursor for the generation of substituted dioxiranes (Adam et al., 1992). Although practical considerations preclude the application of many of these types of structures for bleaching kraft pulps, the incorporation of a ketone recovery system after dioxirane bleaching (Forber, 1992) and the possibility of developing a more effective bleaching agent for kraft pulp heightened our interest in this research area. To explore the reactivity of alternative dioxiranes towards kraft pulp, we initially examined the use of 2-butanone, 3-pentanone, and cyclopentanone as ketone precursors for in-situ generation of substituted dioxiranes. Kraft softwood pulp was then added to a mixture of the ketone and water. We added to this mixture sodium bicarbonate and peroxymonosulfate in the form of  $K_2SO_4 \bullet KHSO_4 \bullet KHOSO_4$ . The resulting pulp slurry was stirred for 1 h at RT, filtered, washed, and extracted with caustic solution. Since preliminary experiments had suggested that some of the keto-solvents were not effective catalysts for peroxymonosulfate, we elected to employ excessively large charges of the oxidant so as to be able to rank the bleaching efficiency of all ketones examined. The results of our initial studies are summarized in Table 1. Several interesting trends are apparent from these experiments. First, at very high charges, peroxymonosulfate can itself effectively delignify kraft pulps. Of greater practical interest is the observation that the softwood kraft pulp was further delignified and brightened when the bleaching solvent contained either acetone, 2-butanone, or 3-pentanone. These differences were apparent not only after the bleaching experiments but also after each caustic extraction procedure. Interestingly, the improved performance of the ketone catalyzed bleaching properties of peroxymonosulfate become readily apparent even at the relatively high charge of 85% peroxymonosulfate.

Although the enhanced bleaching properties of peroxymonosulfate in the presence of acetone have been reported (Lee, 1993; Ragauskas, 1993), this paper now extends these properties to 2-butanone and 3-pentanone. Presumably, use of these latter two reagents also results in the in-situ formation of substituted dioxiranes which are more effective at removing lignin from kraft pulp than peroxymonosulfate itself. The enhanced delignification of the kraft pulps with either acetone, 2-butanone or 3-pentanone is also

accompanied by increased oxidative degradation of cellulose as observed by the viscosity values for the mixed solvent bleaching systems.

In contrast to these results, the use of cyclopentanone appeared to retard the bleaching properties of caroic acid at either of the two high charges employed. As summarized in Table 1, kraft pulps treated with peroxymonosulfate and cyclopentanone were delignified to a lesser extent than pulps treated only with peroxymonosulfate and water. Although we are uncertain as to the exact factors contributing to this divergence in bleaching properties, it may well be due in part to the differences in the water solubility of the in-situ generated dioxiranes and/or starting keto-reagents. Clearly, if the water solubility of the substituted dioxirane is low, then a portion of the dioxirane would remain in the organic phase and secondary dioxirane decomposition reactions (Fig. 1, pathway B) could reduce bleaching efficiency.

To explore the overall relationship between water solubility of the keto-catalyst and bleaching efficiency of peroxymonosulfate reactions, we repeated the above bleaching reactions with cyclohexanone and tetrahydro-4H-pyran-4-one. Presumably, if water solubility of the starting ketone and/or dioxirane was a principle factor influencing the bleaching properties of cyclopentanone and peroxymonosulfate, then cyclohexanone should yield similar bleaching results since the water solubility of these two ketones is comparable. In contrast, tetrahydro-4H-pyran-4-one is substantially more water soluble and should act as a better bleaching catalyst for peroxymonosulfate.

As summarized in Table 1 the catalytic bleaching properties of cyclohexanone were substantially more effective than those observed for cyclopentanone. This result suggests that water solubility is not the principal factor contributing to the poor bleaching capabilities of cyclopentanone. In contrast to these results, tetrahydro-4H-pyran-4-one was shown to be a very effective bleaching catalyst for peroxymonosulfate. Although several factors may be contributing to the bleaching efficiency of this reagent, presumably its improved water solubility contributes to the enhanced bleaching properties.

To explore the potential application of more reactive dioxiranes for bleaching kraft pulps, we examined the bleaching capabilities of trifluoroacetone/caro's acid as a

bleaching system. Following our standard bleaching procedure, a softwood pulp was treated with peroxymonosulfate employing a 57:1 molar ratio of water to 1,1,1-trifluoroacetone. After oxidative bleaching and caustic extraction, the pulp was analyzed for lignin content and brightness values. This data, summarized in Table 1, indicates that 1,1,1-trifluoroacetone improves the bleaching properties of peroxymonosulfate both in terms of extent of delignification and brightness gains. Nonetheless, comparison of these results against the values obtained from acetone clearly indicates that acetone/water provides a more efficient reagent for catalyzing the bleaching properties of peroxymonosulfate. This result suggests that in-situ generation of a very reactive dioxirane is counter productive for bleaching proposes.

Following these preliminary studies, it was apparent that tetrahydro-4H-pyran-4-one, 1,1,1-trifluoroacetone, acetone, 2-butanone and 3-pentanone could catalyze the bleaching reactions of peroxymonosulfate, although for practical proposes only the latter three ketones were of interest. To determine if these catalytic properties occurred under conditions which are closer to practical applications, we repeated the bleaching reactions employing a 10% charge of peroxymonosulfate. The results of these bleaching studies are summarized in Table 2. Under these conditions the trends that started to become apparent in Table 1 are further amplified. Our experiments suggest that acetone is one of the most effective bleaching catalyst for peroxymonosulfate treatment of softwood kraft pulp followed by 2-butanone and 3-pentanone.

#### **4. Conclusions**

It has been shown that several keto-compounds can act as catalysts for bleaching reactions with peroxymonosulfate. The use of keto-compounds, such as 1,1,1-trifluoroacetone which have been reported to yield more reactive dioxiranes than DMD, failed to enhance the overall bleaching process. These results suggest that the effectiveness of a given ketone to enhance bleaching reactions appears to be influenced by its water solubility properties and its intrinsic reactivity. Presumably, the reactivity and water solubility of dimethyldioxirane and acetone correspond well to the requirements for

bleaching kraft pulps with dioxirane reagents.

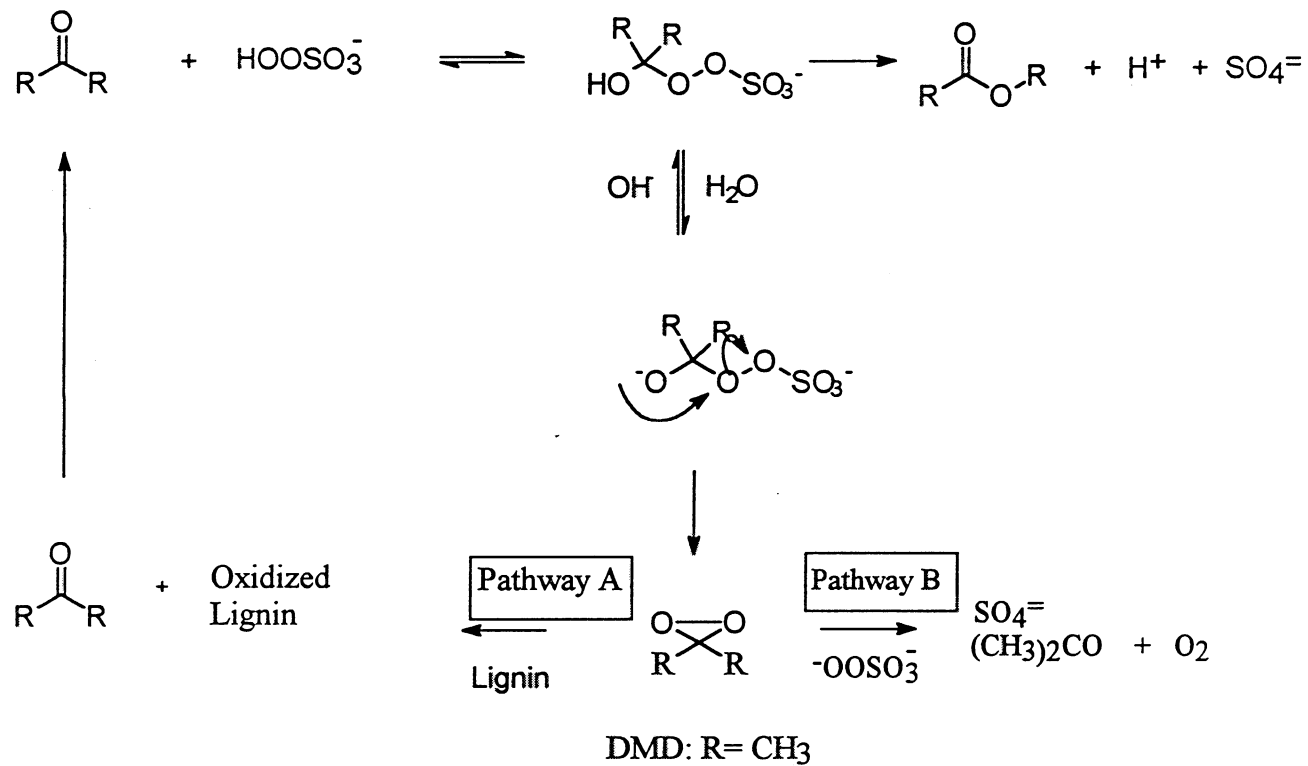


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Figure 1: Overview of DMD Generation and Oxidation Chemistry.



**Table 1.** Bleaching softwood kraft pulp with *in-situ* generated dioxiranes<sup>a</sup>.

<u>Ketone</u>	<u>Chemical Charge of</u>	<u>Fiber Properties of the Bleached/Extracted Pulps</u>		
	<u>Peroxymonosulfate<sup>b</sup></u>	<u>Kappa #</u>	<u>Brightness</u>	<u>Viscosity/cp</u>
-	0%	26.3	23.2	41.9
-	250%	7.3/4.4	49.8/54.1	34.3/23.6
-	85%	15.1/14.5	32.5/34.2	34.2/26.8
Acetone	250%	2.7/1.8	60.3/64.8	22.3/17.1
	85%	5.2/3.4	50.2/53.7	27.7/25.7
2-Butanone	250%	2.4/2.2	61.8/66.1	---/17.8
	85%	5.3/4.0	50.5/53.2	31.6/30.3
3-Pentanone	250%	2.8/1.7	66.7/69.4	16.5/15.1
	85%	6.9/5.6	45.9/50.2	30.7/30.9
Cyclopentanone	250%	16.4/12.2	32.8/34.7	23.0/20.7
	85%	19.4/19.0	26.7/28.3	34.4/33.2
Cyclohexanone	85%	10.6/10.0	34.0/33.8	----
Tetrahydro-4H-pyran-4-one				
	85%	---/2.4	---/55.2	---/20.5
Trifluoroacetone	85%	---/5.1	---/50.4	----

<sup>a</sup>the first value given in each column was determined after bleaching, the second value was determined after bleaching and caustic extraction; <sup>b</sup>charge is based on the weight of peroxymonosulfate employed/weight of pulp, oven dry.

**Table 2.** Bleaching softwood kraft pulp<sup>a</sup> with a 10% charge of peroxymonosulfate and water/ketone solvent mixtures.

<u>Ketone</u>	<u>Fiber Properties of the Bleached/Extracted Pulps</u>	
	<u>Kappa #</u>	<u>Brightness</u>
Acetone	12.5.6/10.1	35.0/36.9
2-Butanone	14.6/12.2	32.4/34.1
3-Pentanone	18.0/16.6	29.8/29.8

<sup>a</sup>see Table 1 for a complete description of the softwood kraft pulp.

