

## Short Communications

## Kinetics of the Decomposition of Aqueous Chlorine Dioxide Solutions

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Chlorine dioxide is used extensively in the pulping industry as a bleaching agent. The industrially-prepared chlorine dioxide always contains some chlorine. During the bleaching almost half the chlorine dioxide is consumed by the unwanted side reaction<sup>1</sup>



It is known that the presence of chlorine and increased pH accelerates the decomposition,<sup>2</sup> but no kinetic studies on chlorine dioxide decomposition under the conditions prevailing during pulp bleaching could be found in the literature. Previous studies are limited to alkaline solutions, room temperature and/or very high chlorine dioxide concentrations.

In the present investigation, the kinetics of aqueous chlorine dioxide decompositions were studied under the conditions used in chlorine dioxide bleaching (temperature 40–80°C, pH 2–7,  $\text{ClO}_2$  conc. = 0.001–0.01 mol/l, total chlorine conc. = 0–0.01 mol/l), but in the absence of pulp.

During each experiment the temperature and pH were kept constant, the latter by successive alkali additions controlled by a pH-stat. The reaction was monitored by removing samples after different reaction times. The chlorine dioxide concentration was determined spectrophotometrically using a Bausch and Lomb 600 instrument.<sup>3</sup> Mainly the initial rate,  $r_0 = -(\text{d}[\text{ClO}_2]/\text{d}t)$  at  $t=0$ , was studied. The reaction mixture was obtained by diluting chlorine dioxide

and "chlorine" stock solutions with distilled water.

The chlorine dioxide stock solution was prepared by absorbing chlorine dioxide gas in water. The chlorine dioxide gas was obtained as follows. Gaseous chlorine was absorbed in a solution of sodium chlorite. When the reaction was complete, as indicated by a change of colour from brown to yellow, the chlorine dioxide was driven off in a stream of nitrogen. The molar ratio chlorine dioxide/total chlorine (*i.e.*  $\sum \text{Cl}_2 + \text{HOCl} + \text{OCl}^-$ ) was larger than 30 in the chlorine dioxide stock solution. The "chlorine" stock solution contained mainly HOCl and was prepared by absorbing chlorine in aqueous NaOH.

As a rule the chlorine dioxide concentration decreased according to a first order reaction. At pH values higher than 6, the "normal" decomposition was followed, after an induction period of up to 60 min, by a very rapid reaction, the rate of which,  $\text{d}[\text{ClO}_2]/\text{d}t$ , was denoted  $r_r$ . This rapid reaction had been previously observed by Rapson.<sup>4</sup> The nature of this autocatalytic reaction is obscure but it can be triggered by injecting minute amounts of 0.1 M HOCl into neutral or slightly alkaline chlorine dioxide solutions. Increased pH increased the rate of this rapid reaction in the absence of "chlorine" as well as that of the initial reaction in the presence of "chlorine". In the absence of chlorine, the pH seemed to have no significant effect on the initial rate of reaction (Fig. 1).

The initial rate of chlorine dioxide decomposition could be described by

$$r_0 = - \frac{\text{d}[\text{ClO}_2]}{\text{d}t} = k_1[\text{ClO}_2] + k_2[\text{ClO}_2][\text{ClO}^-]$$

At 78°C, the temperature at which most of the experiments were carried out,  $k_1 = 3.0 \times 10^{-6} \text{ s}^{-1}$  and  $k_2 = 36 \text{ l mol}^{-1} \text{ s}^{-1}$  were obtained using a value for the equilibrium constant

$$K_a = [\text{ClO}^-][\text{H}^+]/[\text{HClO}]$$

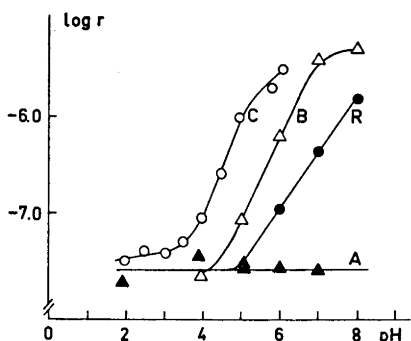
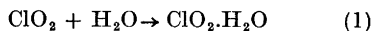


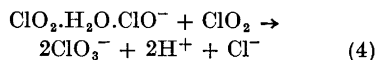
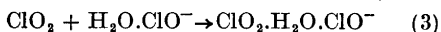
Fig. 1. An example of the effect of pH and the presence of "chlorine" ( $\text{Cl}_2 + \text{HOCl} + \text{OCl}^-$ ) on the rate of decomposition of aqueous chlorine dioxide solutions. The logarithm of the reaction rate in mol/s is plotted versus pH. Temp.  $78^\circ\text{C}$ .  $[\text{ClO}_2] = 0.0028$  mol/l. The initial rate of decomposition  $r_0$ , at different "chlorine" concentrations: A ( $\blacktriangle$ )  $< 1 \times 10^{-4}$ , B ( $\triangle$ )  $2 \times 10^{-4}$ , C ( $\circ$ )  $1.5 \times 10^{-3}$  mol/l; as well as the rate  $r_s$ , of the rapid reaction R ( $\bullet$ ), that occurs after an induction period, are given.

of  $1.59 \times 10^{-7}$  mol/l according to Flis.<sup>10</sup> Both rate constants have activation energies of about 45 kJ/mol. If the temperature dependence of the equilibrium  $\text{ClO}^-/\text{HClO}$  is neglected,  $k_2$  has an apparent activation energy of 70 kJ/mol. The rate equation proposed here, for conditions prevailing during chlorine dioxide bleaching, is different from those previously proposed for chlorine dioxide degradation under other conditions.<sup>3-7</sup>

The first term in the rate equation found can be described by the reactions



while the second term is described by



The reactions (1) and (3) are assumed to be slow and rate determining. This hypothesis is supported by the observation that the entropy of activation,  $\Delta S^\ddagger$ , for the chlorine dioxide decomposition is negative  $-200$  J/K, mol in the absence and  $-100$  J/K, mol in the presence of "chlorine". The entropy values observed

are typical for association reactions of the type (1) and (3).<sup>11</sup>

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## Structural Studies of the *Klebsiella* O Group 8 Lipopolysaccharide

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Five of the twelve different *Klebsiella* O groups contain D-galactose as the only sugar in the O-specific side chains of their lipopolysaccharides (LPS).<sup>1</sup> We have reported structural studies of three of these, O groups 1 and 6<sup>2</sup> (identical) and O group 9.<sup>3</sup> We now report similar studies of the O group 8 LPS.