

- (22) A similar polymer-metal interaction has been proposed to explain the facile decarbonylation of an attached Co complex [G. Gubiltosa, M. Boldt, and H. H. Brintzinger, *J. Am. Chem. Soc.*, **99**, 5174 (1977)].
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- (24) J. Lorntson, J. R. Katzer, and J. M. Schultz, paper presented at the 175th National Meeting of the American Chemical Society, Anaheim, Calif., March 1978.
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## Mechanisms of Chlorine Oxidation of Hydrogen Peroxide

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**Abstract:** Kinetic parameters for two-electron oxidation of hydrogen peroxide by hypochlorous acid have been determined. Reaction with HOCl proceeds according to the rate law  $d[O_2]/dt = k_2[HOCl][H^+][Cl^-]$ ; with  $OCl^-$  ion,  $d[O_2]/dt = k_3[H_2O_2][OCl^-]$ . For the alkaline ( $k_3$ ) pathway, the primary yield of electronically excited oxygen was measured by chemical trapping with 2,5-dimethylfuran (DMFu); results indicate essentially 100% initial formation of ( $^1\Delta$ ) $O_2$ . The rate law for reaction with HOCl is identical with that found for halogenation of DMFu and other reactive organic molecules and, possibly, for conversion of HOCl to  $Cl_2$ . Kinetic arguments are presented supporting the view that these reactions proceed by rate-limiting formation of a common reactive intermediate whose stoichiometry is  $H_2OCl_2$ . From consideration of available thermodynamic parameters, molecular mechanisms and activated complex geometries for the various pathways are proposed.

### Introduction

Oxidation of hydrogen peroxide by hypochlorite ion forms electronically excited molecular oxygen.<sup>1,2</sup> The reaction has been used extensively as a source of  $^1\Delta$  oxygen both for analytical<sup>3</sup> and synthetic purposes,<sup>4</sup> and has been proposed to play a central role in biological disinfection processes.<sup>5</sup>

In 1947, Connick made a careful study of the reaction in acidic aqueous media.<sup>6</sup> In addition to providing a kinetic description of hydrogen peroxide oxidation by molecular chlorine, he was able to detect two additional pathways, one identified as the hydrogen peroxide-hypochlorite ion reaction and another whose rate law and reaction stoichiometry were only ill defined. The  $H_2O_2-Cl_2$  reaction has been given alternative mechanistic interpretations;<sup>6,7</sup> observation of chemiluminescence arising from radiative deactivation of singlet oxygen produced in the reaction has been claimed,<sup>8</sup> but could not be reproduced.<sup>9</sup> More recently, Kajiwara and Kearns have reported results from a cursory study of the reaction in alkaline solution<sup>9</sup> for which apparently straightforward overall second-order kinetics were observed in  $H_2O$ , but quite complex kinetic behavior was noted in  $D_2O$ . Chemiluminescence measurements allowed identification of the  $H_2O_2-OCl^-$  pathway as the origin of singlet oxygen; the product yield could not be established.

With the intention of clarifying these points we have undertaken a rigorous examination of the redox reactions. From the results described herein it has proved possible to draw numerous mechanistic inferences regarding the nature of the activated complexes associated with the various pathways. Additionally, based upon our perception of a reactive intermediate common to several diverse reactions involving hypochlorous acid, we propose what is hopefully a useful unifying view of these reactions.

### Experimental Section

**Reaction Rates and Stoichiometries.** The reactions of hypochlorous acid with hydrogen peroxide and 2,5-dimethylfuran (DMFu) were studied using a variable speed drive assembly<sup>10</sup> coupled to 0.1-1.0-cm optical cells in a Cary 16 recording spectrophotometer. Loss of  $OCl^-$

ions was followed at 290 nm,<sup>11</sup> loss of DMFu at 215 nm, and appearance and decay of intermediates in the DMFu oxidation reaction at 240 nm. Additional measurements of the relatively rapid  $H_2O_2-OCl^-$  reaction were made on a Gibson-Durrum stopped-flow instrument. Oxygen concentrations were measured polarographically using a Clark-type oxygen electrode (Yellow Springs Instrument Co., Model YS-4004). The electrode was inserted into a Pyrex-jacketed cell (Figure 1) maintained at constant temperature by the circulation of water from a thermostated bath through the jacket. Response was monitored with a 1-mV recorder interfaced to the electrode by the circuit shown in Figure 1. The instrument was calibrated by the injection of a known volume of oxygen-saturated or air-saturated solvent, and by the addition of hydrogen peroxide followed by catalase.<sup>12</sup> The system response was tested under a variety of conditions and no deviations from linearity were found for the pH and salt concentrations used in the experiments. Changes in sensitivity with solvent composition and temperature were dealt with by recalibration. Oxygen formation rates were determined by injection of hypochlorite reagent into hydrogen peroxide solutions which had previously been deoxygenated by bubbling with nitrogen. Concentrations were adjusted to ensure that electrode response times were not rate limiting.

Stoichiometries for the  $H_2O_2-HOCl$  reaction were established by determination of oxygen yields, by determination of chloride ion formation using an ion-selective electrode, and by standard iodometric titration.<sup>13</sup> For the last method, known quantities of reactants were mixed with hydrogen peroxide in slight excess. Hydrogen peroxide remaining after reaction ceased was determined by  $I_2$ -thiosulfate titration. Reactant concentrations for kinetic runs were determined by direct iodometric titration and/or absorption spectrometry.

**Determination of  $^1\Delta$ -Oxygen Yields by Chemical Trapping.** Singlet oxygen yields were measured by determining the extent of  $O_2$  trapping by acceptor molecules accompanying chlorine oxidation of  $H_2O_2$ . Assuming the mechanism given in Scheme I, fractional yields of singlet oxygen initially formed ( $Y_1$ ) are given by  $Y_1 = k_i/(k_i + k_{ij})$ . Yields of  $AO_2$  formed during reaction ( $Y_{AO_2}$ ) depend both upon  $Y_1$  and upon partitioning of the intermediate over its various decomposition pathways, steps iii-v, i.e.,  $Y_{AO_2} = Y_1[k_{iv}[A]/(k_{ij} + k_{iv}[A] + k_v)]$ . In reciprocal form,  $Y_{AO_2}^{-1} = Y_1^{-1}(1 + \beta/[A])$ , where  $\beta = (k_{ij} + k_v)/k_{iv}$ . The equations are formally analogous to those used in analysis of photosensitized generation of singlet oxygen;<sup>3b,14</sup> measurement of  $Y_{AO_2}$  as a function of  $[A]$  permits determination of  $Y_1$ .

The compound 2,5-dimethylfuran was chosen as chemical trapping

**Table I.** Stoichiometry of the H<sub>2</sub>O<sub>2</sub>-HOCl Reaction

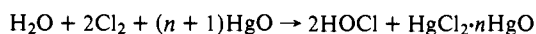
pH	method	ratio
<b>A. In H<sub>2</sub>O, 0.1 M PO<sub>4</sub><sup>3-</sup> Buffer, 0.1 M Cl<sup>-</sup></b>		
3.75	O <sub>2</sub> electrode	O <sub>2</sub> :HOCl = 1.04
4.0	O <sub>2</sub> electrode	1.06
<b>B. In H<sub>2</sub>O, 0.1 M PO<sub>4</sub><sup>3-</sup> Buffer, no Cl<sup>-</sup></b>		
3.9	O <sub>2</sub> electrode	O <sub>2</sub> :HOCl = 1.00
5.0	O <sub>2</sub> electrode	0.98
6.0	O <sub>2</sub> electrode	0.97
7.0	O <sub>2</sub> electrode	0.97
7.8	O <sub>2</sub> electrode	1.00
10.3	O <sub>2</sub> electrode	1.02
7.9	Cl <sup>-</sup> electrode	Cl <sup>-</sup> :HOCl = 1.00
7.4	iodometric titration	H <sub>2</sub> O <sub>2</sub> :HOCl = 1.03
9.2	iodometric titration	1.05
10.5	iodometric titration	1.01
11.7 <sub>3</sub>	iodometric titration	1.08
<b>C. In Alcohols</b>		
methanol	iodometric titration	H <sub>2</sub> O <sub>2</sub> :HOCl = 0.98
ethanol	iodometric titration	0.97
2-propanol	iodometric titration	0.96

agent because it exhibits relatively high solubility in aqueous media, high selective reactivity toward <sup>1</sup>Δ-excited molecular oxygen,<sup>15</sup> and low reactivity toward H<sub>2</sub>O<sub>2</sub> and HOCl, at least in alkaline solution. For singlet oxygen trapping experiments using the oxygen electrode, the rate of solution of DMFu required that at least 10 min preequilibration time be taken between addition of DMFu and hypochlorite. Singlet oxygen trapped was calculated from the difference between hypochlorite added and (ground-state) oxygen measured.

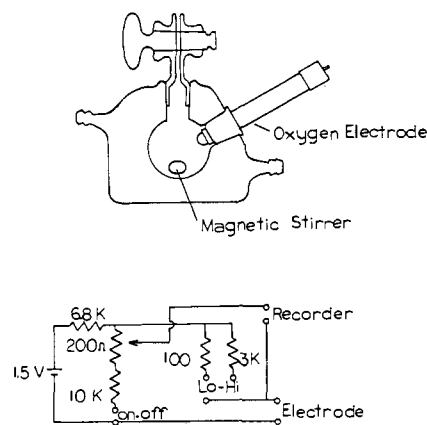
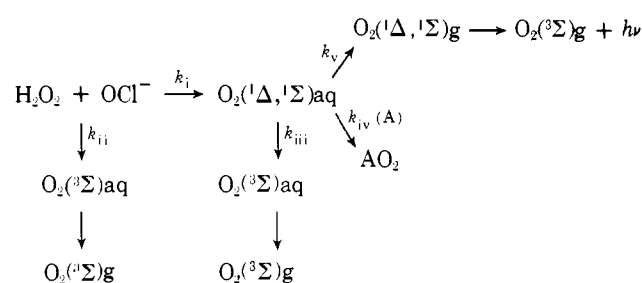
Attempts at determining the extent of DMFu trapping of singlet oxygen using gas chromatographic and spectrophotometric methods were less satisfactory. The acceptor molecule gives strong UV absorption (ε<sub>215</sub> 7900) and is easily resolved on Carbowax or porous polymer columns, allowing for straightforward determination of DMFu concentrations. However, we were unable to identify reaction products by either method, necessitating that yields be inferred from changes in acceptor concentration. For the experimental conditions required, DMFu concentrations undergo relatively small changes during reaction with singlet oxygen. Subsequent manipulative losses stemming from the high volatility of DMFu give rise to relatively large experimental errors; similar experiences have been described by other workers.<sup>14</sup> For this reason, these methods were abandoned in favor of the in situ oxygen measurements. Results obtained by the various methods are qualitatively in accord with one another.

**Photosensitization Studies.** Photosensitization experiments were conducted by measuring the rate of change of oxygen concentration of a solution within the constant-temperature cell containing 10<sup>-6</sup> M methylene blue and various known concentrations of DMFu. The source of illumination was a 200-W lamp placed approximately 4 in. from the cell. By addition of methyl red and methyl orange to the surrounding coolant solution, all but the red light was filtered out. Photolysis of the methylene blue solution in the absence of quenching agent resulted in no significant loss of oxygen.

**Reagents.** Raman infrared analysis of sodium hypochlorite (Mallinckrodt, AR) gave spectral lines characteristic of OCl<sup>-</sup> (713 cm<sup>-1</sup>), ClO<sub>2</sub><sup>-</sup> (790 cm<sup>-1</sup>), and ClO<sub>3</sub><sup>-</sup> (930 cm<sup>-1</sup>) ions; iodometric titrations<sup>13</sup> gave estimated relative concentrations of Cl<sup>-</sup>:ClO<sub>2</sub><sup>-</sup>:ClO<sub>3</sub><sup>-</sup> = 1.0:0.45:10<sup>-3</sup>:0.2. Hypochlorite solutions used in the present studies were therefore prepared by reaction of Cl<sub>2</sub> with HgO<sup>16</sup>, i.e.,

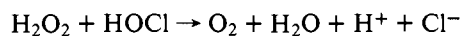


or by vacuum distillation at 40°C of commercial 5% hypochlorite solution acidified to pH 6 with phosphoric acid. The 0.3–0.5 M hypochlorite stock solutions were kept refrigerated and were replaced monthly. Experiments requiring very low chloride ion concentrations were run with either freshly prepared hypochlorite solutions or those previously treated with silver oxide. Commercial 2,5-dimethylfuran was purified by column chromatography over alumina. Methylene blue was purified by literature methods.<sup>17</sup> Water was either twice distilled over alkaline permanganate or purified by reverse osmosis-ion exchange chromatography.

**Figure 1.** Oxygen cell and recorder interfacing circuitry.**Scheme I****Results**

**Notation for Reaction Pathways.** Like Connick,<sup>6</sup> we have found three concurrent redox pathways comprising (formally) hydrogen peroxide oxidation by molecular chlorine, hypochlorous acid, and hypochlorite ion. Inasmuch as these species dominate under strongly acidic, weakly acidic, and neutral to alkaline conditions, respectively, we will refer to the corresponding reactions as the acid, intermediate, and alkaline pathways.

**Reaction Stoichiometries.** Results of the various stoichiometric analyses of the H<sub>2</sub>O<sub>2</sub>-HOCl reactions are summarized in Table I; the data refer to reaction conditions for which either the alkaline (*k*<sub>3</sub>) or intermediate (*k*<sub>2</sub>) pathways predominate. Thus, in contrast to previous reports of excess hypochlorite consumption for the *k*<sub>2</sub> pathway<sup>6</sup> and possibly for the *k*<sub>3</sub> pathway in D<sub>2</sub>O,<sup>9</sup> we find that simple 1:1 stoichiometry is maintained. Previous studies,<sup>18</sup> subsequently confirmed, have shown that the acid (*k*<sub>1</sub>) pathway also obeys this stoichiometry; it is therefore evident that by all pathways the net reaction is



or its equivalent for the other forms of the oxidant (Cl<sub>2</sub>, OCl<sup>-</sup>).

**Rate Law for the Alkaline (*k*<sub>3</sub>) Pathway.** Spectrophotometric and O<sub>2</sub>-potentiometric methods were used to monitor the reaction, the latter method allowing extension of the measurements into weakly acidic media (pH >3, at low chloride ion concentrations) where spectrophotometric methods fail because equilibrium concentrations of hypochlorite ion are undetectably low. All solutions were buffered with phosphate ion; buffer concentrations were adjusted to maintain a constant ionic strength (μ = 0.1 M). Peroxide concentrations were maintained in sufficient excess that first-order conditions obtained; i.e., -d[HOCl]/dt = *k*'[HOCl]<sub>0</sub>. Plots of measured rate constants (*k*') against hydrogen peroxide concentration were linear with intercepts at the origin demonstrating first-order dependence upon [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>, i.e., -d[HOCl]/dt =

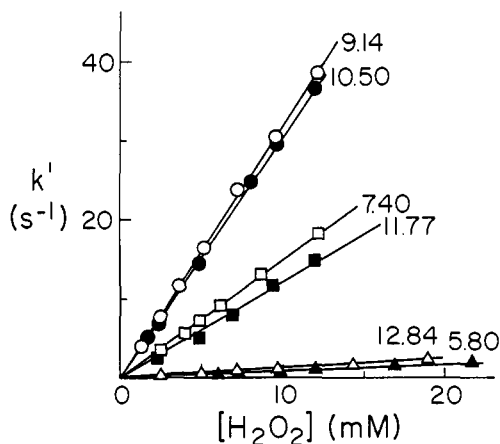


Figure 2. Dependence of the observed rate constant for the alkaline  $\text{H}_2\text{O}_2$ -HOCl reaction upon pH and hydrogen peroxide concentration. Conditions:  $\mu = 0.1$  M (phosphate),  $T = 25^\circ\text{C}$ . Numbers give pH values for the corresponding lines.

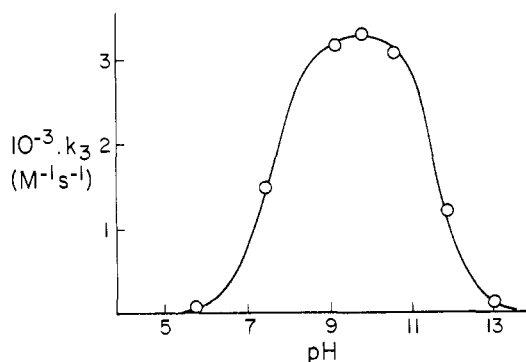
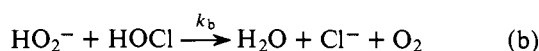
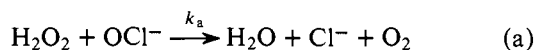


Figure 3. Hydrogen ion dependence of the rate constant for the alkaline  $\text{H}_2\text{O}_2$ -HOCl reaction. Conditions:  $\mu = 0.1$  M (phosphate),  $T = 25^\circ\text{C}$ . Circles, experimental points, representing averages of six to ten individual runs; line, theoretical curve, assuming rate and equilibrium parameters given in the text.

$k_3[\text{H}_2\text{O}_2]_0[\text{HOCl}]_0$ , where  $k' = k_3[\text{H}_2\text{O}_2]_0$  and the subscripts 0 refer to total reactant concentrations. Examination of the pH dependence of the specific rate constant,  $k_3$ , over the range  $3 < \text{pH} < 13$  gave rate behavior indicative of reaction principally through a pathway involving loss of a proton in the activated complex, e.g., either of the reactions



For reaction a,  $k_3 = k_a / (1 + [\text{H}^+]/K_1)(1 + K_2/[\text{H}^+])$ ; for reaction b,  $k_3 = k_b / (1 + K_1/[\text{H}^+])(1 + [\text{H}^+]/K_2)$ ; where  $K_1$  and  $K_2$  are the acid dissociation constants for hypochlorous acid and hydrogen peroxide, respectively. Although the reaction schemes are kinetically indistinguishable, we will present arguments in the Discussion section which favor pathway b, i.e., identification of  $\text{HO}_2^-$  and HOCl as the reactive species.

Data from the spectrophotometric measurements are summarized in Figures 2 and 3. Using literature values<sup>19,20</sup> for  $K_1 = 2.9 \times 10^{-8}$  M,  $K_2 = 2.2 \times 10^{-12}$  M, we calculate for the specific rate constants  $k_a = 3.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_b = 4.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at  $25^\circ\text{C}$ , in good agreement with previous estimated values.<sup>9</sup> The temperature dependence for this reaction, measured by following rates of oxygen evolution, is given in Figure 4. Activation parameters for pathway b, calculated from absolute reaction rate theory, are  $\Delta H^\ddagger = 3.1 \text{ kcal/mol}$  and

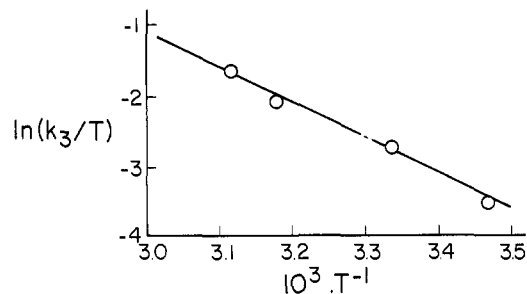


Figure 4. Temperature dependence of the  $k_3$  pathway rate constant. Conditions: 0.1 M (phosphate), pH 5.0.

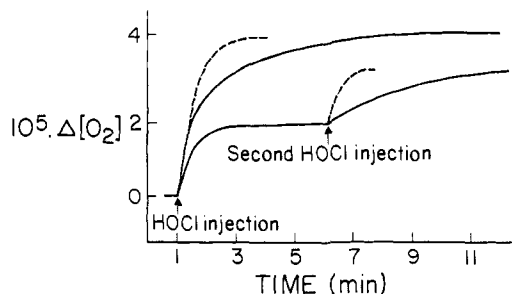
Table II. Specific Rate Constants ( $k_b$ ) for the Alkaline Reaction<sup>a</sup>

medium	method	$10^{-7}k_b$ , $\text{M}^{-1} \text{ s}^{-1}$
pH 4-5, unbuffered, $\mu \approx 10^{-4}$ M, $25^\circ\text{C}$	iodometric titration	$3.2^b$
pH 7-13, unbuffered, $\mu \approx 10^{-4}$ M, $25^\circ\text{C}$	iodometric titration	$\sim 3^c$
pH 5, 0.1 M phosphate, $25^\circ\text{C}$	spectrophotometric	4.2
pH 4, 0.1 M phosphate, $25^\circ\text{C}$	$\text{O}_2$ evolution	4.2
pH 4, 0.025 M acetate, $25^\circ\text{C}$	$\text{O}_2$ evolution	4.3
pH 9.4, 0.1 M acetate, $25^\circ\text{C}$	$\text{O}_2$ evolution	4.2
pH 4, unbuffered, $\mu \approx 10^{-4}$ M, $25^\circ\text{C}$	$\text{O}_2$ evolution	4.6
pH 3.7, unbuffered, $\mu \approx 10^{-4}$ M, $25^\circ\text{C}$	$\text{O}_2$ evolution	4.0
pH 6-12, 0.1 M borate, $0^\circ\text{C}$	manometry	$< 1^d$
pH 9.2, 0.04 M borate, $8^\circ\text{C}$	$\text{O}_2$ evolution	0.46
pH 9.2, 0.04 M phosphate, $8^\circ\text{C}$	$\text{O}_2$ evolution	1.6
pH 9.2, 0.04 M borate, $19^\circ\text{C}$	$\text{O}_2$ evolution	1.7
pH 9.2, 0.04 M phosphate, $19^\circ\text{C}$	$\text{O}_2$ evolution	2.9
pH 9.2, 0.04 M borate, $25^\circ\text{C}$	$\text{O}_2$ evolution	2.5
pH 9.2, 0.04 M phosphate, $25^\circ\text{C}$	$\text{O}_2$ evolution	3.9
pH 4.5, methanol: $\text{H}_2\text{O} = 1:1$	$\text{O}_2$ evolution	$t_{1/2} \approx 60$ s
pH 8.25, methanol: $\text{H}_2\text{O} = 1:1$	$\text{O}_2$ evolution	$t_{1/2} \approx 30$ s
pH 9.0, methanol: $\text{H}_2\text{O} = 1:1$	$\text{O}_2$ evolution	$t_{1/2} \approx 15$ s
ethanol: $\text{H}_2\text{O} = 19:1$	$\text{O}_2$ evolution	$t_{1/2} \approx 10^2$ s
1-propanol	$\text{O}_2$ evolution	$t_{1/2} \geq 10^2$ s
$\text{CCl}_4$	$\text{O}_2$ evolution	$t_{1/2} > 10^3$ s

<sup>a</sup> Unless otherwise indicated, this work. <sup>b</sup> Reference 6. <sup>c</sup> Reference 9. <sup>d</sup> Reference 22.

$\Delta S^\ddagger = -12.5 \text{ eu}$  at  $25^\circ\text{C}$ ; temperature dependence of the acid dissociation constants was taken into account.<sup>20b</sup>

Results of kinetic studies made over a wider range of medium conditions, including the low pH, low chloride measurements with the oxygen electrode, are reported in Table II; specific rate constants ( $k_b$ ) have been calculated assuming that mechanism b is operative. The reaction is insensitive to ionic strength and to the identity of added buffers, with the exception of borate ion, whose presence decreases the reaction rate. Borate ion complexation of hydrogen peroxide is known to occur;<sup>21</sup> the decrease in reaction rate in borate buffers can be quantitatively accounted for by assuming that the borate-peroxide complex is unreactive toward hypochlorite, thereby decreasing the "effective" hydrogen peroxide concentration. The dissociation constant calculated from the rate data is 0.037 M, in agreement with the literature value of 0.03 M.<sup>21</sup> It is also notable that acetate catalysis observed for the acid ( $k_1$ ) pathway<sup>6</sup> does not extend to the alkaline reaction.



**Figure 5.** Oxygen electrode response after injection of HOCl into 1.3 mM  $\text{H}_2\text{O}_2$  solution. Conditions: 4.8 mM NaCl, 0.1 M potassium acid phthalate, pH 4.0, 25 °C. Upper trace:  $[\text{HOCl}]_0 = 3.8 \times 10^{-5}$  M. Lower trace:  $[\text{HOCl}]_0 = 1.5 \times 10^{-5}$  M. Dashed lines give anticipated trace without inhibition.

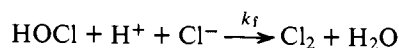
Because the reaction rate shows strong pH dependence, rate variations observed for different solvents are not easily interpreted; in general, the reaction rate was found to decrease markedly with decreasing polarity of the solvent.

**Rate Law for the Acid ( $k_1$ ) Pathway.** The kinetic behavior of this pathway has been described;<sup>6</sup> our measured rates of oxygen evolution were identical with previously cited rates of chlorine disappearance, confirming the rate law.

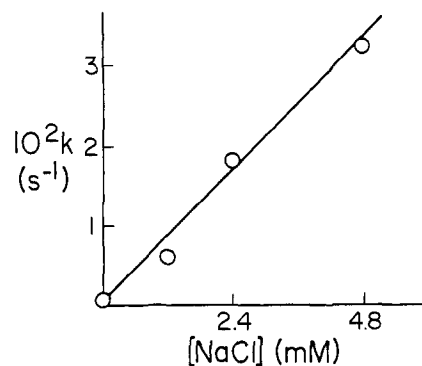
**Rate Law for the Intermediate ( $k_2$ ) Pathway.** When  $[\text{H}^+][\text{Cl}^-] = 10^{-8}$ – $10^{-5}$   $\text{M}^2$ , the total rate of reaction, though quite slow, is significantly higher than accountable by the reactions of chlorine and hypochlorite ion with hydrogen peroxide, i.e., the acid and alkaline pathways. The reaction rate in this region is sensitive to environmental effects, exhibiting buffer catalysis, apparent autoinhibition, and very strong inhibition by certain cations and anions. An extreme example of this behavior is presented in Figure 5.

Reproducible rates not subject to these complicating effects were observed for the early stages of the reactions. The rate law was therefore determined by either measurement of initial rates of oxygen evolution or initial slopes of integrated rate plots made assuming simple first-order behavior. The former method could be used only for absolute rates of oxygen evolution less than ca.  $1.5 \times 10^{-7}$   $\text{M s}^{-1}$ ; otherwise, electrode response was too slow to provide accurate direct measurement of the initial rates. The latter procedure is justified because we had found by the method of initial rates that the concentration dependence of HOCl is first order, concentrations of other reactants were in excess and therefore invariant, and the reaction stoichiometry was unaffected by catalytic and inhibitory rate effects. Excepting the first few points, the first-order plots were linear over 2–3 half-lives. At low oxygen evolution rates the methods gave equivalent results. Significant contributions to the overall rate were made by the  $k_1$  and  $k_3$  pathways; correction for these contributions was made by subtraction of calculated initial rates for the competing reactions under the experimental conditions. The resulting rate law, determined over the concentration ranges  $[\text{H}^+] = (0.1\text{--}2.0) \times 10^{-4}$  M,  $[\text{HOCl}] = (0.5\text{--}4.0) \times 10^{-5}$  M,  $[\text{H}_2\text{O}_2] = (0.7\text{--}8.8) \times 10^{-3}$  M,  $[\text{Cl}^-] = (0.01\text{--}10) \times 10^{-3}$  M, is  $d[\text{O}_2]/dt = k_2[\text{HOCl}][\text{H}^+][\text{Cl}^-]$  with  $k_2 = 3.5 \times 10^4$   $\text{M}^{-2} \text{s}^{-1}$  at 25°C,  $\mu \approx 10^{-3}$  M. Experimental data are given in Figures 6 and 7 and in Table III.

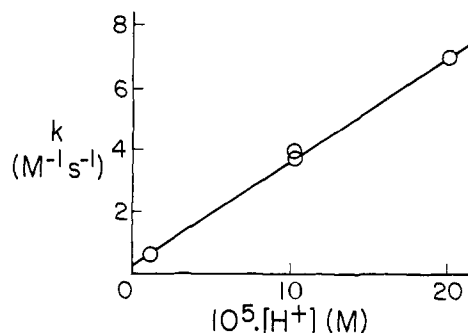
The rate law is nearly identical with that measured for chlorine formation,<sup>23</sup> i.e.



for which  $d[\text{Cl}_2]/dt \approx k_f[\text{HOCl}][\text{H}^+][\text{Cl}^-]$ , with  $k_f = 1.8 \times 10^4$   $\text{M}^{-2} \text{s}^{-1}$  at 20°C,  $\mu = 0.1$  M. To investigate the possibility that the intermediate pathway might arise simply from the  $\text{H}_2\text{O}_2\text{--Cl}_2$  reaction which is rate limited by the slow conversion

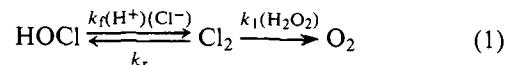


**Figure 6.** Chloride ion dependence of reaction by intermediate ( $k_2$ ) pathway. Rate constants,  $k$ , determined from initial oxygen evolution rates using  $d[\text{O}_2]/dt = k[\text{HOCl}]_0$ . Conditions: 1.3 mM  $\text{H}_2\text{O}_2$ , pH 3.68, 25 °C.



**Figure 7.** Hydrogen ion dependence of reaction by the intermediate ( $k_2$ ) pathway. Experimental points represent averages over three to five individual runs. Rate constants,  $k$ , calculated from initial oxygen evolution rates using  $d[\text{O}_2]/dt = k[\text{Cl}^-][\text{HOCl}]_0$ .

of HOCl to  $\text{Cl}_2$ , we examined the following reaction scheme:<sup>24</sup>



Using the known rate parameters<sup>6,23</sup> and experimental conditions, we found that the calculated rates of  $\text{O}_2$  evolution were at least  $10^2$ -fold too low to account for the measured evolution rates; our numerical calculations were confirmed by displaying the data on an analog computer. It is evident, therefore, that the  $k_2$  pathway corresponds to peroxide oxidation by a chemical intermediate whose composition is given by the rate law and whose formation is rate limiting.

Efforts to eliminate autoinhibition by reagent purification were unsuccessful; the effect is diminished substantially by using meticulously cleaned glassware, suggesting that inhibition is somehow dependent upon the surface of the reaction vessel. Autoinhibitory effects were not influenced by the addition of sodium salts of chlorite, chlorate, perchlorate, sulfate, or phosphate ions, or by the presence of oxygen in the reaction solution. However, a strong cation dependence was evident, lithium ion causing strong inhibition and potassium ion causing slight inhibition relative to sodium ion. Silver and mercury salts did not appreciably alter the reaction rates. Further, the extent of these inhibitory effects was inversely dependent upon the concentrations of hydrogen peroxide and chloride ions, reaction by the  $k_2$  pathway in solutions containing  $[\text{H}_2\text{O}_2]$  or  $[\text{Cl}^-] > 4 \times 10^{-3}$  M showing negligible inhibition.

The effects of acetate and phthalate buffers on the reaction rate are complicated. Catalysis of the  $k_2$  pathway occurs at high concentrations of hydrogen peroxide, but is apparently compensated for by opposing inhibitory effects at lower peroxide concentration levels. Thus, for instance, at pH 4 with

Table III. Rate Constants ( $k_2$ ) for the Intermediate Reaction

$10^5[\text{HOCl}], \text{M}$	$[\text{H}_2\text{O}_2], \text{mM}$	$[\text{Cl}^-], \text{mM}$	$10^5[\text{H}^+], \text{M}$	$10^7$ initial rate $R_0, \text{M s}^{-1}$	$10^7 R_3,^a \text{M s}^{-1}$	$10^7 R_1,^b \text{M s}^{-1}$	$10^{-4} k_2,^c \text{M}^{-2} \text{s}^{-1}$
2	1.32	4.86	20	6.44	0.144	0.113	3.2
2	1.32	4.86	20	6.40	0.144	0.113	3.2
2	1.32	2.43	20	3.7	0.139	0.059	3.6
2	1.32	1.21	20	1.16	0.135	0.030	1.91
2	1.32	1.21	20	1.08 <sup>d</sup>	0.135	0.030	1.73
2	4.4	1.2	10	1.60	0.986	0.047	2.34
2	4.4	2.41	10	3.02	1.02	0.091	3.98
2	8.8	1.2	10	2.52	1.97	0.114	1.82
2	1.32	4.82	10	4.48	0.317	0.053	4.24
2	1.32	4.82	10	4.08	0.317	0.053	3.82
2	1.32	4.86	10	4.34	0.29	0.058	4.1
1	1.32	4.86	10	1.93	0.195	0.029	3.5
4	1.32	4.86	10	9.2	0.58	0.116	4.4
2	0.66	4.82	0.85	2.60 <sup>e</sup>	2.1	0.0	6.1
2	0.66	4.82	0.85	2.38 <sup>f</sup>	1.75	0.0	7.0
2	0.66	9.65	0.85	3.2 <sup>f</sup>	1.75	0.0	8.8

<sup>a</sup> Calculated from  $R_3 = k_3[\text{H}_2\text{O}_2][\text{OCl}^-]$ . <sup>b</sup> Calculated from  $R_1 = k_1[\text{H}_2\text{O}_2][\text{Cl}_2]$ . <sup>c</sup> Calculated from  $k_2[\text{HOCl}][\text{H}^+][\text{Cl}^-] = R_0 - R_3 - R_1$ . <sup>d</sup> Direct measurement; all other rates determined by extrapolation of integrated rate data to  $t = 0$ . <sup>e</sup> 0.1 M phosphate buffer. <sup>f</sup> 0.025 M phosphate buffer.

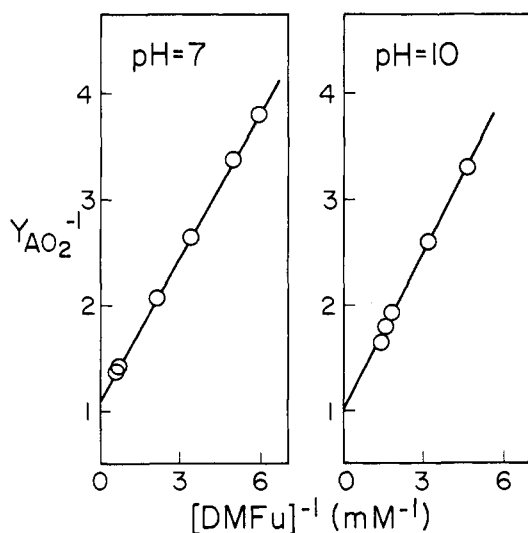


Figure 8. Competitive quenching of singlet oxygen. Conditions: 0.1 M phosphate, 25 °C,  $[\text{HOCl}]_0 = 1.6 \times 10^{-5} \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 4.4 \text{ mM}$ .

$[\text{H}_2\text{O}_2] = 4.4 \times 10^{-3} \text{ M}$ ,  $[\text{Cl}^-] = 2.4 \times 10^{-3} \text{ M}$ , a ca. fivefold increase in initial rate is measured in 0.025 M acetate buffer over the unbuffered reaction, whereas with  $[\text{H}_2\text{O}_2] = 1.3 \times 10^{-3} \text{ M}$ ,  $[\text{Cl}^-] = 4.8 \times 10^{-3} \text{ M}$  only a ca. 20% increase is observed. With phthalate buffers the effects appear to be even more marked (Figure 5).

**Singlet Oxygen Yields for the Alkaline Pathway.** Representative data from chemical trapping experiments are given in Figure 8. For all runs, 2,5-dimethylfuran concentrations were in sufficient excess to ensure that the factor  $\beta/(A)$  remained constant over the course of the reaction. In general, both intercepts ( $Y_1^{-1}$ ) and slopes ( $Y_1^{-1}\beta$ ) of the double reciprocal plots are independent of medium conditions in the domain where the alkaline pathway predominates.

Quenching ratios ( $\beta \approx 5.5 \times 10^{-4}$ ) were slightly higher than the  $\beta$  value determined by photosensitization methods ( $\beta = 3 \times 10^{-4}$ ) for identical medium conditions. The latter number is identical with cited  $\beta$  values<sup>15</sup> for methylene blue sensitized singlet oxygen formation. The discrepancy in values in the two reactions may reflect differences in deactivation by escape into the gaseous phase (step v in Scheme I); molecular oxygen is

evolved in the peroxide oxidation reaction, but is only consumed in the photochemical experiments. The alternative possibility that the presence of photosensitizer dye might alter relative rates of physical and chemical deactivation of "nascent" singlet oxygen seems less likely on the basis of other studies which gave identical  $\beta$  values for  $\text{H}_2\text{O}_2/\text{OCl}^-$  and photoinitiated oxygenations.<sup>14</sup> Conditions for which hypochlorite consumption was extremely rapid (high  $\text{H}_2\text{O}_2$  concentrations, pH 8–9.5) gave  $\beta$  values greater than those routinely encountered. The effect is likely ascribable to incomplete mixing of reactants giving rise to localized depletion of the trapping agent with attendant increases in measured  $\text{O}_2$  yields.<sup>4a</sup> At considerably reduced hypochlorite reduction rates (low peroxide, low pH), the  $\beta$  value undergoes an apparent decrease. This effect is artifactual, and arises from the direct reaction of hypochlorite with dimethylfuran. Not only are oxygen yields reduced in the presence of DMFu under these conditions, but the apparent rate constant for  $\text{O}_2$  evolution also increases. Since the HOCl-DMFu reaction does not produce oxygen, this increase can only be attributed to competition between reductants for HOCl. Kinetic characterization of the HOCl-DMFu reaction is described below; decreases in oxygen yields in quenching experiments at low hypochlorite reduction rates can be quantitatively accounted for by this reaction.

Extrapolated singlet oxygen yields ( $Y_1$ ) are insensitive to the apparent variations in  $\beta$  values at the extreme reaction rates; results indicate essentially quantitative formation of singlet oxygen in the  $\text{H}_2\text{O}_2\text{-OCl}^-$  reaction. Quenching experiments were also made for  $\text{H}_2\text{O}_2$  oxidation by  $\text{OCl}^-$  in aqueous alcoholic mixtures and by  $\text{Cl}_2\text{O}$  in (nearly) anhydrous organic solvents; singlet oxygen yields measured in this and other studies<sup>4a,14</sup> are compiled in Table IV. Results cited for the organic media are only tentative since possible complications arising from the  $\text{Cl}_2\text{O-DMFu}$  reaction have not been considered and apparent acidities are unknown.

**Hypochlorous Acid Oxidation of Dimethylfuran.** Interference in the quenching experiments by direct reaction of HOCl with the chemical trapping agent becomes progressively greater with increasing acidities. Disappearance of DMFu exhibits complex kinetic behavior, highly dependent upon medium conditions and characterized by the formation and slow decay of unstable intermediate species. Nonetheless, under experimental conditions encompassing the trapping experiments, the rate law could be cast in simple form, i.e.,

Table IV. Singlet Oxygen Yields in Organic Solvents

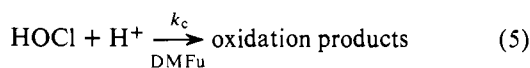
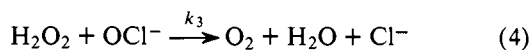
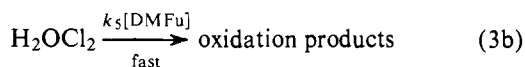
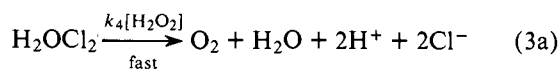
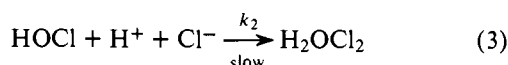
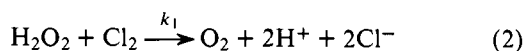
solvent	$Y_1$	
	this work	ref 4a
methanol-H <sub>2</sub> O (1:1), pH 8.25	0.9	
<i>tert</i> -butyl alcohol-H <sub>2</sub> O <sub>2</sub> (1:1)		<0.1
methanol ([OH <sup>-</sup> ] = 0.012 M)		0.4-0.8 <sup>a</sup>
ethanol-H <sub>2</sub> O (19:1)	0.6-0.7	
methanol	0.6	>0.6
ethanol	0.7-0.8	>0.6
2-propanol		>0.4
<i>tert</i> -butyl alcohol		<0.1
methanol- <i>tert</i> -butyl alcohol (1:1)		0.4-0.65 <sup>a</sup>
acetonitrile		<0.1
tetrahydrofuran		<0.1
dioxane		<0.1
carbon tetrachloride	0.2	

<sup>a</sup> Yield decreased with increasing temperature.

$-d[\text{DMFu}]/dt = (k_c + k_d[\text{Cl}^-])[\text{HOCl}][\text{H}^+]$ , with  $k_c = 93 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_d = 4.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$  at 25°C,  $\mu \approx 10^{-3} \text{ M}$ . The rate law term for the chloride-dependent pathway,  $k_d[\text{HOCl}][\text{H}^+][\text{Cl}^-]$ , is identical with that for the HOCl-H<sub>2</sub>O<sub>2</sub> reaction, i.e.,  $k_d \approx k_2$ , implying that the two reactions occur by rate-limiting formation of a common intermediate.

**Chemical Trapping Experiments for the Intermediate ( $k_2$ ) Pathways.** Using procedures analogous to those described for the alkaline reaction we measured oxygen yields in solutions containing reactants and DMFu (Table V). Conditions were adjusted to optimize reaction by the intermediate pathway, e.g., at pH 4.0, with  $[\text{Cl}^-] = 7 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 0.018 \text{ M}$ , 47% total reaction occurred through the intermediacy of H<sub>2</sub>OCl<sub>2</sub>.

The following concurrent reactions were considered in analyzing the data:



Under the experimental conditions HOCl was concentration limiting; the fractions of the total reaction proceeding by any of the pathways can therefore be had from the ratios of the pseudo-first-order rate constants,<sup>25</sup> e.g., for pathway 3 the ratio is  $k_2'/\Sigma k_i$ , where  $\Sigma k_i = k_1' + k_2' + k_3' + k_c'$ . Oxygen is formed by pathways 2 and 4 and, partially, by pathway 3, depending upon the partitioning of the intermediate between steps  $k_4$  and  $k_5$ . Since reaction of H<sub>2</sub>OCl<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> yields O<sub>2</sub>, whereas reaction with DMFu does not, measurement of oxygen yields provides information on the relative reaction rates of the reductants with the intermediate. Because any singlet oxygen initially formed in the H<sub>2</sub>OCl<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> reaction will be partially trapped by reaction with DMFu, these experiments can also, in principle, measure the extent of singlet oxygen formation by the  $k_2$  pathway.

Measured oxygen yields were corrected for oxygen formed

Table V. Oxygen Yields for the Intermediate Pathway<sup>a</sup>

run	$[\text{O}_2 \text{ measd}]/[\text{HOCl}]_0$	$10^4[\text{A}], \text{ M}$	$[(k_1' + k_3')/\Sigma k_i][\beta/[\text{A}]]/(1 + \beta/[\text{A}])$	$[\text{O}_2(\text{cor})]/[\text{HOCl}]_0$
1	0.30	1.9	0.28	0.02
2	0.25	2.4	0.26	-0.01
3	0.25	2.8	0.24	0.01
4	0.22	2.8	0.24	-0.02
5	0.11	5.4	0.18	-0.07
6	0.10	5.7	0.18	-0.08
7	0.16	3.3	0.22	-0.06
8	0.14	3.0	0.24	-0.10

<sup>a</sup> At pH 4.0,  $[\text{Cl}^-] = 7.0 \times 10^{-3} \text{ M}$ ,  $[\text{H}_2\text{O}_2] = 0.018 \text{ M}$ ,  $T = 25^\circ \text{C}$ . For these conditions, rates by pathways 2-5 are  $R_2 = k_1'[\text{HOCl}] = 0.0061[\text{HOCl}]$ ,  $R_3 = 0.0294[\text{HOCl}]$ ,  $R_4 = 0.0177[\text{HOCl}]$ ,  $R_5 = 0.0093[\text{HOCl}]$ ;  $(k_1' + k_3')/\Sigma k_i = 0.38$ ,  $\beta = 5.0 \times 10^{-4}$ .

Table VI. Thermodynamics of Hydrogen Peroxide Oxidation by Chlorine<sup>a</sup>

reaction	$-\Delta G^\circ$ , kcal/mol <sup>b</sup>	$-\Delta H^\circ$ , kcal/mol
$\text{Cl}_2 + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{Cl}^-$	32.8	28.3
$\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{H}^+ + \text{Cl}^- + \text{H}_2\text{O}$	37.4	34.8
$\text{OCl}^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + \text{Cl}^- + \text{H}_2\text{O}$	47.6	38.0
$\text{OCl}^- + \text{HO}_2^- \rightarrow \text{O}_2 + \text{Cl}^- + \text{OH}^-$	44.4	32.9
$\text{HOCl} + \text{HO}_2^- \rightarrow \text{O}_2 + \text{Cl}^- + \text{H}_2\text{O}$	53.3	43.1

<sup>a</sup> Calculated from data given in ref 39 and D. D. Perrin, "Dissociation Constants of Inorganic Acids and Bases in Aqueous Solution", IUPAC publication, Butterworths, London, 1969. <sup>b</sup> At 25°C.

by the acid and alkaline pathways using the equation

$$\frac{[\text{O}_2(\text{cor})]}{[\text{HOCl}]_0} = \frac{[\text{O}_2(\text{measd})]}{[\text{HOCl}]_0} - \left( \frac{k_1' + k_3'}{\Sigma k_i} \right) \left[ \frac{\beta/[\text{A}]}{1 + \beta/[\text{A}]} \right]$$

The ratio,  $\beta/[\text{A}]/(1 + \beta/[\text{A}])$ , represents the fraction of singlet oxygen initially formed that is not chemically trapped by DMFu. It is tacitly assumed that reaction by the acid pathway gives rise to formation of singlet oxygen, although this is not known. Since reaction by this pathway comprises less than 10% of the total decomposition of HOCl, any errors introduced by the assumption are minor.

Results of the calculations given in Table V indicate that all the oxygen formed can be accounted for by the acid and alkaline reactions, hence that, by the  $k_2$  pathway, DMFu apparently competes effectively with H<sub>2</sub>O<sub>2</sub> for the intermediate, H<sub>2</sub>OCl<sub>2</sub>. Therefore, no information concerning singlet oxygen formation in the latter reaction can be had from these experiments.

**Singlet Oxygen Studies for the Acid ( $k_1$ ) Pathway.** Molecular chlorine reacts prohibitively rapidly with known water-soluble trapping agents, precluding their use in singlet oxygen quenching experiments. No chemiluminescence was visible in this reaction domain even at optimal peroxide decomposition rates.

## Discussion

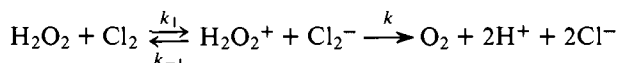
**Geometries of Activated Complexes.** Thermodynamic parameters for reaction by the different pathways are given in Table VI. In each instance reactions are sufficiently exothermic to allow direct formation of molecular oxygen in its <sup>1</sup>Δ electronic state. (Lowest excited states of O<sub>2</sub> are <sup>1</sup>Δ and <sup>1</sup>Σ, 22 and 38 kcal/mol, respectively, above the ground (<sup>3</sup>Σ) state.<sup>3</sup>) Because reactions by the various pathways are all highly exergonic, the rate constants are not likely to be strongly influenced by relative driving forces.<sup>27</sup> In this regard, note that the relative rates do not vary systematically with reaction free energies (cf.

the reaction between  $\text{OCl}^-$  and  $\text{HO}_2^-$  which is undetectably slow, even in strongly alkaline solution where these ions are the dominant species (Figure 3)).

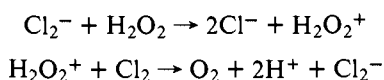
The diverse kinetic behavior can be rationalized if it is assumed that reaction takes place by nucleophilic attack by peroxide upon the chlorine atom, forming, e.g., for the alkaline pathway, an activated complex whose geometry is  $[\text{HO}_2\text{-Cl-OH}]^-$ . Though unstable, this complex bears formal resemblance to the well-described trichloride ion.<sup>28</sup> Two-electron transfer leads directly to the reaction products with both atoms of molecular oxygen being derived from the peroxide.<sup>29</sup> Conservation of spin momentum requires that the oxygen product be singlet as is the case for the alkaline pathway.

The  $\text{HO}_2^-$  ion is strongly nucleophilic, as judged by its dynamic behavior toward electrophilic organic substrates,<sup>30</sup> whereas  $\text{H}_2\text{O}_2$  exhibits only weakly nucleophilic character. In HOCl, the chlorine atom is electropositive;<sup>31-33</sup> polarization is weakened by removing a proton or substituting  $\text{Cl}^-$  for the  $\text{OH}^-$  ion. Therefore, the energetically least demanding means of reaching an activated complex for the redox reaction would seem to be by nucleophilic attack of  $\text{HO}_2^-$  upon HOCl at the electrophilic chlorine atom. For each of the other pathways the chlorine species ( $\text{OCl}^-$ ,  $\text{Cl}_2$ ) is a weaker electrophile<sup>34</sup> and/or the attacking hydrogen peroxide is a poorer nucleophile. An additional factor mitigating against formation of the activated complex from  $\text{OCl}^-$  and  $\text{HO}_2^-$  is the electrostatic repulsion encountered by the like-charged ions. Two additional points are worth emphasizing: (1) that the species we identify as reactive by the  $k_3$  pathway ( $\text{HO}_2^-$ , HOCl) are not the ones that predominate in solution ( $\text{H}_2\text{O}_2$ ,  $\text{OCl}^-$ ) and, therefore, that pathway b (Results section) is preferred, and (2) that our postulations are consistent with previously proposed mechanisms for the acid pathway(s) in which a HOCl intermediate is thought to form by nucleophilic displacement of  $\text{Cl}^-$  by  $\text{H}_2\text{O}_2$ .<sup>6,29</sup>

**The  $\text{H}_2\text{O}_2\text{-Cl}_2$  Reaction—Molecular vs. Free-Radical Mechanisms.** A free-radical mechanism for peroxide decomposition by the acid pathway has been proposed,<sup>7</sup> the essential feature of which is sequential one-electron transfers from peroxide to chlorine species as in the following equations:



In order to derive the experimental rate law, it was necessary to assume that chain-propagating steps, e.g.,

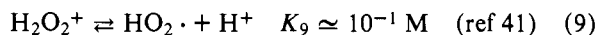
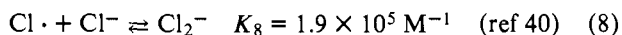
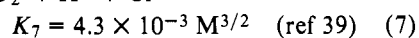
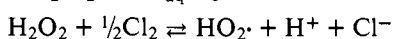
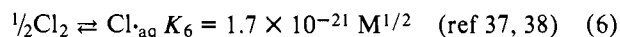


are insignificant. From published kinetic data,<sup>36</sup> the value for the radical-initiating step was calculated to be  $k_1 = 1.9 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . This mechanism provides an attractive explanation for the apparent absence of chemiluminescence in reaction by the acid pathway since stepwise electron transfer would allow direct formation of ( $^3\Sigma$ ) $\text{O}_2$  without violation of spin conservation requirements. However, as discussed above, there is no reason to suspect that formation of  $^1\Delta$  oxygen is energetically restrictive (Table VI).

In any event, the mechanism can be shown to be incorrect. The equilibrium constant for the first electron transfer step

$$K = k_1/k_{-1} = (\text{H}_2\text{O}_2^+)(\text{Cl}_2^-)/(\text{H}_2\text{O}_2)(\text{Cl}_2)$$

can be calculated from the following thermodynamic data:



for which  $K = K_6K_7K_8/K_9 \approx 1.4 \times 10^{-17}$ . To account for these thermodynamic properties, the rate constant  $k_{-1} = k_1/K \approx 10^{19} \text{ M}^{-1} \text{ s}^{-1}$ , far too large to be physically attainable. It is clear, then, that any potential free-radical mechanism must include chain-propagating steps. In testing numerous reaction schemes, we have not found such a mechanism capable of reproducing the experimental rate law. Therefore, there are presently no plausible arguments favoring the intermediacy of radical species in this reaction.

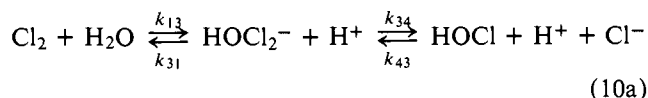
**Relative Chemiluminescence Yields.** Assuming that singlet-excited oxygen is formed in the  $\text{H}_2\text{O}_2\text{-Cl}_2$  reaction, how can we explain the absence of detectable chemiluminescence? Maximal steady-state concentrations of  $^1\Delta$  oxygen can be estimated from a simple kinetic model comprising its exponential growth and decay, i.e., for the acid pathway,

$$[\text{O}_2(^1\Delta)]_{\text{max}} = (k_1'[\text{HOCl}]_0/(k_\tau - k_1'))(\exp(-k_1 t_{\text{max}}) - \exp(-k_\tau t_{\text{max}}))$$

where  $t_{\text{max}}$  is the time after mixing corresponding to the maximal concentration of  $\text{O}_2(^1\Delta)$ ,  $k_1' = k_1[\text{H}_2\text{O}_2]_0$  and  $k_\tau = 1/\tau$ , with  $\tau = 2 \mu\text{s}$  being the lifetime of  $\text{O}_2(^1\Delta)$  in aqueous solution.<sup>42</sup> An equivalent expression holds for the alkaline ( $k_3$ ) pathway. Values of  $t_{\text{max}}$  are found by evaluating the first derivative of the equation at  $d[\text{O}_2(^1\Delta)]/dt = 0$ . For the conditions of the chemiluminescence experiments  $[\text{Cl}_2] \approx [\text{OCl}^-] \approx 1 \text{ M}$ ,  $[\text{H}_2\text{O}_2] \approx 10 \text{ M}$ , the ratio of maximal singlet oxygen concentrations by the two pathways is  $[\text{O}_2(^1\Delta)]_{k_1}/[\text{O}_2(^1\Delta)]_{k_3} \approx 0.06$ . Since visible chemiluminescence occurs principally by dimol emission,<sup>2</sup> intensities are proportional to the square of  $^1\Delta$  concentrations.<sup>43</sup> Relative intensities for the two pathways are calculated to be  $I_{k_1}/I_{k_3} \approx 0.004$ . An alternative model based upon the observation that dimol emission occurs from the gas phase<sup>44</sup> and, therefore, that ( $^1\Delta$ ) $\text{O}_2$  concentrations should be roughly proportional to oxygen evolution rates gives equivalent results. Neither calculation should be taken literally since, at the high concentrations of reactants used, the rapid reaction rates encountered obviate any attempts at achieving homogeneous mixing. It is evident even from this crude analysis, however, that chemiluminescence intensities for the  $\text{H}_2\text{O}_2\text{-Cl}_2$  reaction cannot exceed ca. 1% of the intensities attainable by the alkaline pathway.

**The Intermediate ( $k_2$ ) Pathway—Evidence for a “Chlore-noid” Mechanism.** The rate law for the DMFu-HOCl reaction is consistent with rate data for HOCl oxidation of other similarly reactive organic molecules; in particular, the term  $k_2(\text{HOCl})(\text{H}^+)(\text{Cl}^-)$  is commonly found.<sup>32,45,46</sup> The observation that DMFu competes effectively with  $\text{H}_2\text{O}_2$  for HOCl (Table V) under conditions where  $\text{H}_2\text{O}_2$  is oxidized by the chemical intermediate,  $\text{H}_2\text{OCl}_2$ , implies that DMFu also reacts with this species (eq 3). As discussed in greater detail below, a self-consistent view of the various reactions of HOCl demands this conclusion. Halogenation of the other organic molecules described by the  $k_2$  rate law may also involve reaction with  $\text{H}_2\text{OCl}_2$ , rather than prior dehydration to  $\text{Cl}_2$  as has been proposed.<sup>45</sup>

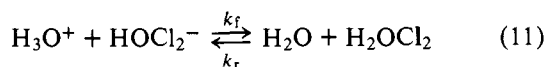
We believe that chlorine hydrolysis (eq 10) also proceeds by rate-limiting formation of this same intermediate. Eigen and Kustin<sup>23</sup> have interpreted their kinetic data for this reaction in terms of the following scheme:



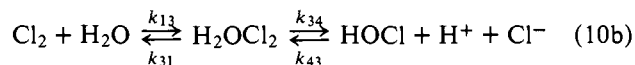
(rate constants refer to their notation). Alternative pathways were excluded on the basis of kinetic and thermodynamic arguments. The intermediate,  $\text{HOCl}_2^-$ , was not observed, but its existence is consistent with other kinetic data<sup>47</sup> and is



structurally analogous to other, stable halogen species, e.g., the trichloride ion.<sup>28</sup> We differ with Eigen and Kustin on the following point. They assert that proton transfer to  $\text{HOCl}_2^-$ , i.e.



is energetically favorable, hence, rapid;<sup>26</sup> we feel that reaction 11 is energetically unfavorable in the direction written and, therefore, that proton transfer to  $\text{HOCl}_2^-$  is necessarily slow. The mechanistic consequence of this interpretation is the recognition of  $\text{H}_2\text{OCl}_2$  as the least stable intermediate, viz., the reaction scheme:



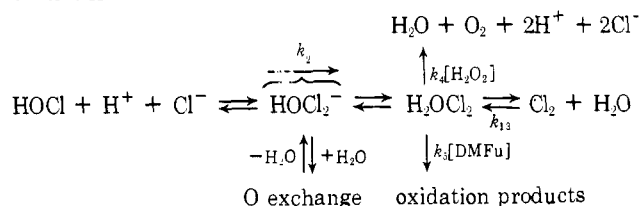
The elementary step identified by  $k_{43}$  now refers to  $\text{H}_2\text{OCl}_2$  formation; by their analysis,  $k_{43} \approx 2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ , identical with  $k_2$  within the limits of the estimation.<sup>48</sup>

Some indication of the relative strengths of the bases in eq 11 can be had from consideration of the hypochlorous acidium ion dissociation constant, i.e.,  $K_a = [\text{HOCl}][\text{H}^+]/[\text{H}_2\text{OCl}^+]$ . Estimates based upon various thermodynamic approximations vary widely, from  $\text{p}K_a \approx -3$  to  $\text{p}K_a \approx -26$ ;<sup>49</sup> by basing his calculation upon the reasonable assumption that relative base strengths of  $\text{H}_2\text{O}$  and  $\text{HOCl}$  should be proportional to those of  $\text{OH}^-$  and  $\text{OCl}^-$ , Hine<sup>50</sup> calculated a value of  $K_a \approx 10^{10} \text{ M}$ . Comparison with the analogous constant for dissociation of the hydronium ion,  $K_a' = [\text{H}_2\text{O}][\text{H}^+]/[\text{H}_3\text{O}^+] = 55 \cdot \text{M}$ , reveals the enormous base-weakening effect of chlorine substitution for hydrogen on oxygen. Although addition of a chloride ion in forming  $\text{HOCl}_2^-$  will increase basicity at the oxygen atom, it seems unlikely that total compensation can be achieved.

The inhibitory and catalytic effects observed in the  $\text{H}_2\text{O}_2$ - $\text{HOCl}$  reaction by the  $k_2$  pathway are reminiscent of similar reports by Connick<sup>6</sup> and Kajiwara and Kearns,<sup>9</sup> in the latter instance for the alkaline reaction in  $\text{D}_2\text{O}$ . Although considerably more work will be required to identify sources of these effects, several points are worth mentioning. First, the reaction stoichiometry remains unaltered, even under conditions of strong inhibition of rates. It is clear, therefore, that intermediates ultimately react to give  $\text{O}_2$  product. Second, apparent surface effects may relate to borate inhibition of the alkaline pathway, especially since the effects are diminished at high concentration levels of  $\text{H}_2\text{O}_2$ . Third, the rate-enhancing effects of acetate and phthalate buffers may well arise by general acid catalysis, which would be expected for rate-limiting proton transfer as we have proposed for formation of the reactive  $\text{H}_2\text{OCl}_2$  intermediate.

In their study of oxygen exchange between  $\text{HOCl}$  and  $\text{H}_2\text{O}$ , Anbar and Taube<sup>47</sup> found a chloride-catalyzed pathway proceeding according to the equation rate =  $k_{\text{OH}}[\text{HOCl}][\text{Cl}^-]$ , with  $k_{\text{OH}} = 1.7 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ . One homeomorphic form is rate =  $k'_{\text{OH}}[\text{H}_2\text{OCl}_2][\text{OH}^-]$ ; although this form suggests the possibility of rate-limiting  $\text{OH}^-$  attack on  $\text{H}_2\text{OCl}_2$ , the mechanism cannot be correct because it requires  $k'_{\text{OH}} = k_{\text{OH}}k_{34}/k_{43}K_w \approx 10^{16} \text{ M}^{-1} \text{ s}^{-1}$ ,<sup>48</sup> which is physically unattainable. The original interpretation<sup>47</sup> of solvent displacement of  $\text{OH}^-$  on the intermediate ion,  $\text{HOCl}_2^-$ , seems most likely. Kinetics of chlorine exchange between  $\text{HOCl}$  and  $\text{Cl}^-$  has also been reported;<sup>51</sup> for this reaction, rate =  $k_{\text{Cl}}[\text{HOCl}][\text{H}^+][\text{Cl}^-]$ , with  $k_{\text{Cl}} = 5.3 \times 10^{11} \text{ M}^{-2} \text{ s}^{-1}$ . From comparison of  $k_{\text{Cl}}$  with  $k_2$  ( $k_{\text{Cl}}/k_2 \approx 10^7$ ), it is clear that  $\text{Cl}$  exchange does not await the relatively slow formation of the  $\text{H}_2\text{OCl}_2$  species involved in the redox reactions. In fact, the rate law defies interpretation in terms of formation of simple intermediates. The hypochlorous acidium ion,  $\text{H}_2\text{OCl}^+$ , is far too unstable to be kinetically significant and, for reaction to proceed through the

## Scheme II



intermediacy of  $\text{HOCl}_2^-$ , the equilibrium defined by  $K = [\text{HOCl}_2^-]/[\text{HOCl}][\text{Cl}^-]$  must be greater than ca.  $10 \text{ M}^{-1}$ . Even presuming this possibility, it is difficult to understand the dynamic function of the proton, i.e., what basis is there for the apparent lack of chlorine exchange in the equilibrium,  $\text{HOCl} + \text{Cl}^- \rightleftharpoons \text{HOCl}_2^-$ , without proton addition?

The reactions of hypochlorous acid, as we have interpreted the data, are summarized in Scheme II. A likely geometry for the intermediate in the chlorine hydrolysis reaction is  $\text{H}_2\text{O}-\text{Cl}-\text{Cl}$ . The  $\text{Cl}-\text{O}$  bond is considerably weakened by the two bound protons, leading to facile dissociation of  $\text{H}_2\text{O}$ . The central chlorine atom is also electron deficient and is activated both toward reduction and electrophilic insertion into electron-rich bonds by protonation on oxygen. In this latter regard, the behavior of the intermediate can be thought to parallel that proposed for insertion reactions involving electrophilic oxygen (oxenoid mechanism)<sup>52</sup> and carbon atoms (carbenoid mechanism).<sup>53</sup> Oxygen exchange does not require prior protonation of the hydroxyl group presumably because, unlike dehydration of  $\text{H}_2\text{OCl}_2$  to form  $\text{Cl}_2$ , the energy required to weaken the  $\text{Cl}-\text{O}$  scissile bond in reaching the transition state is compensated for by bond formation to the incoming solvent molecule.

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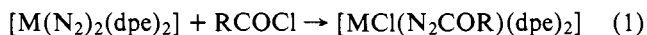
## Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. 8.<sup>1</sup> Diazoalkane Complexes of Molybdenum and Tungsten

Masanobu Hidai,\* Yasushi Mizobe, Maki Sato, Teruyuki Kodama, and Yasuzo Uchida

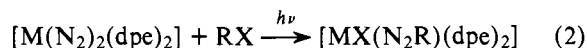
Contribution from the Department of Industrial Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. Received January 25, 1978

**Abstract:** The hydrazido(2-) complexes  $[\text{M}(\text{NNH}_2)(\text{dpe})_2][\text{BF}_4]$  (M = Mo or W, dpe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) obtained from *trans*- $[\text{M}(\text{N}_2)_2(\text{dpe})_2]$  and HBF<sub>4</sub> in THF readily condense with a variety of aldehydes and ketones to produce a new series of diazoalkane or hydrazone-type complexes  $[\text{M}(\text{N}-\text{N}=\text{CRR}')(\text{dpe})_2][\text{BF}_4]$  in good yields. This reaction is remarkably accelerated in the presence of a trace of an acid. The structure of the diazoalkane complex  $[\text{W}\{\text{N}=\text{C}(\text{CH}_3)-\text{CH}_2\text{COCH}_3\}(\text{dpe})_2][\text{BF}_4] \cdot \text{THF}$  has been determined from three-dimensional x-ray counter data. The complex crystallized in space group  $P\bar{1}$  with  $a = 13.577$  (15),  $b = 21.440$  (25),  $c = 11.204$  (13) Å;  $\alpha = 102.36$  (3),  $\beta = 100.00$  (3),  $\gamma = 70.27$  (5)°;  $V = 2980.5$  (58) Å<sup>3</sup>; and  $Z = 2$ . The coordination geometry about the tungsten atom is octahedral with the diazoalkane ligand and fluoride anion in a *trans* position. The W-N-N linkage is essentially linear and the angle N-N-C is 125.2 (19)°. The W-N, N-N, and N-C distances are 1.770 (17), 1.317 (25), and 1.300 (30) Å, respectively. The methyl group attached to the C=N bond is held in a distorted sandwich position relative to two phenyl groups, which accounts for the unusually higher shift of the methyl resonance in the <sup>1</sup>H NMR spectrum.

The formation of carbon-nitrogen bonds from coordinated dinitrogen is an important elementary step for the direct conversion of dinitrogen into organonitrogen compounds. The first examples of formation of organonitrogen ligands from coordinated dinitrogen were found in the reaction of organic acid halides with  $[\text{M}(\text{N}_2)_2(\text{dpe})_2]$  (1) (M = Mo or W, dpe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>) and  $[\text{ReCl}(\text{N}_2)(\text{PMe}_2\text{Ph})_3\text{L}]$ , which yielded acyl- and aroyldiazenido complexes as shown in the equation<sup>2</sup>



Following this discovery, two groups independently found the alkylation reactions of coordinated dinitrogen in molybdenum and tungsten dinitrogen complexes 1 with alkyl halides to form alkyldiazenido complexes.<sup>2b,3,4</sup>



X-Ray structural analyses of  $[\text{MoCl}(\text{N}_2\text{COPh})(\text{dpe})_2]$ <sup>5</sup> and  $[\text{Mo}(\text{N}_2\text{C}_6\text{H}_{11})(\text{dpe})_2]$ <sup>3</sup> clearly showed that these complexes contained a carbon-nitrogen bond with an essentially linear Mo-N-N group. However, analogous acyl-, aroyl-, or alkyl-diazenido complexes have not yet been obtained from dinitrogen complexes with monophosphines  $[\text{M}(\text{N}_2)_2\text{L}_4]$  (M = Mo or W, L = monoteriary phosphine). The reaction of  $[\text{M}(\text{N}_2)_2(\text{PMe}_2\text{Ph})_4]$  with methyl bromide yields, for instance,  $[\text{MBr}_4(\text{PMe}_2\text{Ph})_2] + 2\text{N}_2$ , and there is no sign of alkylated nitrogen-containing products.<sup>6</sup>

Recently we briefly described a new potential method for making carbon-nitrogen bonds from coordinated dinitrogen which consists of two steps, i.e., the formation of a hydra-