Reaction of Methanol with Chlorate Ions in Acid Solution Containing Hg^{+2} by NMR

William R. Ernst, Bhart Indu, and Brian Crump
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332

Leslie T. Gelbaum
Research Center for Biotechnology, Georgia Institute of Technology, Atlanta, GA 30332

The reaction rate of methanol was measured in solutions of sodium chlorate and sulfuric acid at several levels of temperature and concentration, in the presence of mercuric nitrate. The progress of the reaction was monitored by proton NMR signals corresponding to methanol and formic acid. Chlorine dioxide formation was suppressed by adding mercuric nitrate, which was shown earlier to catalyze the disproportionation of the intermediate species, chlorous acid, and sequester chloride ions. The reaction is first order in methanol and chlorate concentration and in the Hammett acidity function. The reaction of formic acid, sodium chlorate and sulfuric acid was also studied using the same technique. Formic acid was stable and did not react with chlorate at a measurable rate, even at concentrations and temperatures of a commercial process. This study relates to commercial processes that produce chlorine dioxide by reducing chlorate ions with methanol.

Introduction

Chlorine dioxide is an oxidizing chemical that is used in water purification and is replacing chlorine in many chemical bleaching processes because of environmental concerns. The literature contains numerous articles on chlorine dioxide research (for example, Rapson, 1956, 1958; Lenzi and Rapson, 1962; Hong et al., 1967; Masschelein, 1979). This work continues our recent study of reactions that are important in the commercial production of chlorine dioxide (Burke et al., 1993; Ernst et al., 1988; Hoq et al., 1991a,b,c, 1992a,b; Indu, et al., 1991a,b, 1993; Indu, 1993). These articles also provide background on chlorine dioxide uses and manufacture.

Many commercial chlorine dioxide facilities reduce sodium chlorate with methanol in sulfuric acid solution in a well-mixed reaction vessel that operates under steady-state conditions with total recycle of unconverted sodium chlorate. In one type of process, aqueous solutions of the three reactants are continuously fed to a vessel that serves as reactor and evaporative crystallizer. All chlorine dioxide, by-products, unreacted methanol, and water exit the reactor in the vapor phase, except for sodium sesquisulfate, which is crystalline and is removed by filtration. Filtered mother liquor containing unreacted sodium chlorate and sulfuric acid is returned to the reactor.

Indu (1993) used Rapson's general hypothesis (Lenzi and Rapson, 1962) to reduce chlorate by a reducing agent, R,

$$HClO_3 + R \rightarrow HClO_2 + RO \qquad (1)$$

$$HClO_2 + R \rightarrow HClO + RO \qquad (2)$$

$$HClO + R \rightarrow HCl + RO \qquad (3)$$

$$HClO_3 + HCl \rightarrow HClO_2 + HClO \qquad (4)$$

$$HClO_3 + HClO_2 \rightarrow 2ClO_2 + H_2O \qquad (5)$$

$$HCl + HClO \leftrightarrow Cl_2 + H_2O \qquad (6)$$

as a basis for discussing sequences of reactions that might lead to chlorine dioxide in the methanol–chlorate process. (The reactions are not necessarily elementary steps.)

Equations 1 to 3 represent stepwise reduction of chlorate to chloride. In Eq. 4 chloride reacts with chlorate to form chlorous acid and hypochlorous acid. Chlorine dioxide is formed by the stoichiometry in Eq. 5. Hypochlorous acid

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Correspondence concerning this article should be addressed to W. R. Ernst.

formed in Eq. 4 can be reduced to chloride in Eq. 3 and react with chloride in Eq. 6 producing chlorine.

Subsets of the preceding reactions formally describe chlorine dioxide formation.

(a) Equations 3, 4 and 5 represent a chlorine (or HOCl)–chloride cycle in which chlorine dioxide is produced by the reaction of chloride and chlorate. Lenzi and Rapson (1962) presented experimental evidence supporting such a sequence, with sulfur dioxide as the reducing agent. The main function of R is to reduce HOCl in order to regenerate chloride. To start the cycle, they imply that chloride ions must be present, either as an additive or generated by Eqs. 1 to 3. Chlorine losses are a result of Eq. 6, followed by volatilization of chlorine.

(b) Equations 1 and 5 represent a sequence in which the main function of R is to reduce chlorate to chlorous acid. Chlorine dioxide is produced by reaction of chlorous acid and chlorate. Chlorine and chloride are not needed to produce chlorine dioxide; however, these species might be produced by a sequence of "side" reactions—Eqs. 2, 3 and 6.

(c) It is possible that under some conditions of concentration and temperature, neither sequence governs and the overall process depends on contributions from both sequences.

To express these two sequences in terms of the methanol–chlorate-acid system, we must first identify important species that form in this system. Our previous work suggests that methanol is oxidized by chlorate in a stepwise manner, first forming formaldehyde, then formic acid, and finally carbon dioxide. Methanol and formic acid were measured in chlorine dioxide product solutions from commercial plants, confirming that unreacted methanol and formic acid leave the reactor with chlorine dioxide (Hoq et al., 1991a), possibly as methyl formate, which is highly volatile (Indu et al., 1993). In laboratory experiments, we observed that formaldehyde, formic acid, chlorous acid, chloride, and chlorine form when methanol interacts with chlorate in acid solution and that formaldehyde appears in very low concentration under certain conditions, suggesting that it is a short-lived intermediate (Hoq et al., 1991a, 1992b; Indu et al., 1993; Indu, 1993). Formic acid was relatively stable in the solutions, suggesting that it reacts much more slowly than methanol with chlorate.

The results of previous work have identified formaldehyde and formic acid as species that form during the production of chlorine dioxide. The simplest way of representing the chlorine–chloride cycle using these species is

$$\mathrm{HClO + CH_3OH \rightarrow HCl + HCHO + H_2O}, \qquad (7)$$

followed by rapid conversion of formaldehye with hypochlorous acid to form formic acid,

$$\mathrm{HClO + HCHO \rightarrow HCl + HCOOH}. \qquad (8)$$

Both reactions are similar in form to Eq. 3, with CH_3OH and HCHO representing reducing agents, R and R'. These two reactions represent an oxidation-reduction sequence. Equations 4 and 5 complete the cycle by regenerating hypochlorous acid and producing chlorine dioxide, respectively. These four reactions are sometimes combined with Eq. 6 and written as a two-reaction sequence,

$$\mathrm{CH_3OH + 2Cl_2 + H_2O \rightarrow 4HCl + HCOOH} \qquad (9)$$

$$\mathrm{2HClO_3 + 2HCl \rightarrow 2ClO_2 + Cl_2 + 2H_2O}. \qquad (10)$$

Indu (1993) cited an experimentally determined rate expression for the reduction of chlorine by methanol that suggests Eq. 9 might be too slow compared to the overall formation rate of chlorine dioxide to support the sequence given earlier.

The alternative sequence that does not involve chloride or chlorine as intermediates can be represented in its simplest form as

$$\mathrm{H^+ + CH_3OH + ClO_3^- \rightarrow HClO_2 + HCHO + H_2O}, \qquad (11)$$

followed by the rapid conversion of formaldehyde by reaction with chlorate to form formic acid,

$$\mathrm{H^+ + HCHO + ClO_3^- \rightarrow HClO_2 + HCOOH}. \qquad (12)$$

Both reactions are similar in form to Eq. 1, with CH_3OH and HCHO representing reducing agents, R and R'. These two reactions represent an oxidation-reduction sequence. To form chlorine dioxide, chlorous acid must react with chlorate according to Eq. 5. A fourth reaction, between formic acid and chlorate to form carbon dioxide, was not included because our previous work and the present work indicate that this reaction is insignificant.

Indu (1993) assumed this alternative subset, and studied the overall rate of chlorine dioxide formation in the methanol–chlorate-acid system in flow reaction experiments. He correlated the data by a power law expression,

$$\text{Rate, } \mathrm{ClO_2}\ (\mathrm{M/min}) = 3.3\times10^{14} \exp(-27{,}303/RT) \times [\mathrm{NaClO_3}]^{1.14}[\mathrm{CH_3OH}]^{1.12}\, h_-^{2.15}. \qquad (13)$$

In this expression, an acidity function, h_-, was used instead of acid concentration. (Values of this function were first determined by Cox and McTigue (1964) for sulfuric acid solutions. Indu's flow reactor studies were conducted in both sulfuric acid solutions and in mixtures of sulfuric acid and sodium sulfate. Indu et al., 1991b, modified the acidity function so that it represents the acidity of such mixtures. They also conducted batch reactor experiments at 25°C and obtained similar orders of reaction (0.93, 1.54, and 2.25 order, respectively, in methanol, chlorate, and h_-). They proposed a mechanism involving two protons that is consistent with the approximate first-order dependence in methanol and chlorate and second order in acidity function. In some of the studies, Indu analyzed reaction liquid for chloride and gaseous product for chlorine. He found that chloride ranged from 0.008 to 0.05 M. Chlorine averaged about 3.7% of the chlorine dioxide produced. It has been reported that chlorine levels are considerably less in commercial plants.) These species were not considered in his kinetic analysis because they were assumed to be produced by side reactions that were not coupled to the main reaction sequence. Further work may be required to verify this assumption.

In this work, we studied the rate of what may be the primary methanol-consuming reaction of the chlorine dioxide process, Eq. 11. This work was facilitated by the finding (Indu, 1993) that mercuric ions catalyze the disproportionation of chlorous acid and decomposition of chlorine dioxide in solutions that contain chlorous acid. By incorporating mercuric nitrate into reaction solutions, we are able to eliminate secondary reactions involving methanol. Analysis of methanol is complicated by the presence of chlorine dioxide in solution. By incorporating mercuric nitrate into reaction solutions, chlorine dioxide is eliminated, greatly facilitating the analysis of methanol. The reaction experiments were carried out in a nuclear magnetic resonance (NMR) tube. The progress of the reaction was monitored by measuring the proton signal for methanol and comparing it to the proton signal for a nonreacting reference standard, cyclohexane.

Experimental Procedure

The reaction of methanol, sodium chlorate, and sulfuric acid was studied using the following procedure. Known volumes of 9-M sulfuric acid, 6-M sodium chlorate, D_2O, and 0.4-M mercuric nitrate solutions were added to a 5-mm NMR tube, using an autoclavable adjustable volume pipetter (Eppendorf—Model 4810, with accuracies of 1.6% for dispensed volumes between 100 and 1,000 μL, and up to 2% for 10–100 μL to obtain required mixture concentrations. The tube was placed in the NMR instrument (a Varian XL-400 Fourier-transform spectrometer) and heated to the desired temperature using the temperature control system of the instrument. The solution was scanned once and the water signal assigned a decoupler offset. This offset was used in kinetics experiments to suppress the water signal.

After a preliminary scan of the sample was completed, the NMR tube was withdrawn from the instrument for a period of 30 s, during which time methanol (8 μL of 2-M methanol solution) was added using an autoclavable adjustable volume pipetter (Eppendorf—Model 4710 with accuracy of 6% at 2 μL and 1.2% at 10 μL), and the tube was shaken five times. The addition of methanol resulted in a total volume of 500 μL of reaction solution. The solution cooled slightly during this 30-s period. The tube was returned to the instrument and the solution was scanned after the temperature had reached about 95% of the control temperature. Each concentration measurement required four proton-NMR scans of the sample to obtain a satisfactory signal-to-noise ratio. We were somewhat restricted in the number of scans since the components were changing rapidly with time. It took approximately 22 s for each scan (2 s for acquisition and 20 s for relaxation time), for a total of 88 s for each concentration measurement. For each experiment, the starting point ($t = 0$) corresponds to the midpoint of the first series of four scans.

The reaction of formic acid with sodium chlorate and sulfuric acid was also studied in a few experiments using the procedure just given. In those experiments, formic acid was added to the reaction solution instead of methanol. Mercuric nitrate was not needed in these experiments because formation of chlorine dioxide (as judged by color change of the solution) was not fast enough to be a concern.

Stock solutions of 9-M sulfuric acid, 2-M methanol, and 6-M sodium chlorate were prepared from certified or certified ACS Fisher reagents. A 0.4-M mercuric nitrate solution was prepared by dissolving 13.73 g mercuric nitrate (Fisher certified ACS) in 100 mL of distilled water containing 2 mL of 2-M nitric acid (Fisher reagent ACS). A 2.36-M formic acid solution was prepared from 23.6-M (Fisher certified ACS) formic acid. The deuterium oxide, D_2O, was purchased from the Aldrich Chemical Company.

The NMR apparatus and procedures, including temperature equilibration experiments, are detailed in the Appendix.

Table 1. Experimental Conditions and Rate Constants*

Exp No.	Temp. °C	Hg^{2+} M	ClO^{3-} M	H_2SO_4 M	$-H_0$	h_0	$k' \times 10^3$ Exp. s^{-1}	$k \times 10^5$ Exp. $1/(s \times M^2)$	$k \times 10^5$ Calc. $1/(s \times M^2)$
1	21.2	0.016	2.4	3.0	1.365	23.17	0.47	0.85	0.78
2	21.2	0.016	2.4	3.0	1.365	23.17	0.37	0.66	0.78
3	21.2	0.016	2.0	2.5	1.107	12.80	0.27	1.07	0.78
4	21.2	0.016	3.0	2.5	1.107	12.80	0.28	0.73	0.78
5	21.2	0.016	2.0	3.5	1.610	40.75	0.57	0.70	0.78
6	21.2	0.016	3.0	3.5	1.610	40.75	1.10	0.90	0.78
7	24.5	0.016	0.63	3.5	1.610	40.75	0.25	0.97	1.05
8	24.5	0.016	1.0	3.5	1.610	40.75	0.42	1.03	1.05
9	24.5	0.016	1.58	3.5	1.610	40.75	0.67	1.05	1.05
10	24.5	0.016	2.51	3.5	1.610	40.75	1.32	1.29	1.05
11	34	0.016	3.0	3.5	1.610	40.75	2.70	2.21	2.38
12	34	0.016	2.0	3.5	1.610	40.75	1.62	1.99	2.38
13	34	0.016	3.0	2.5	1.107	12.80	0.95	2.48	2.38
14	34	0.016	2.0	2.5	1.107	12.80	0.54	2.09	2.38
15	40	0.016	2.0	1.69	0.662	4.60	0.24	2.61	3.89
16	40	0.016	2.0	2.32	1.011	10.26	0.80	3.87	3.89
17	40	0.016	2.0	3.0	1.365	23.17	1.56	3.37	3.89
18	40	0.016	2.0	3.73	1.719	52.31	4.40	4.21	3.89
19	48	0.016	2.4	3.0	1.365	23.17	4.38	7.88	7.28
20	48	0.016	2.4	3.0	1.365	23.17	4.13	7.43	7.28
21	48	0.016	2.4	3.0	1.365	23.17	4.89	8.79	7.28
22	48	0.032	2.4	3.0	1.365	23.17	4.56	8.20	7.28
23	48	0.064	2.4	3.0	1.365	23.17	4.40	7.91	7.28

*Initial methanol concentration in all experiments = 0.032 ± 0.004 M.

Results

NMR analyses

A total of 23 experiments were conducted to study the reaction of methanol, sodium chlorate, and sulfuric acid. Table 1 lists conditions of each experiment. The temperatures include 21.2, 24.5, 34, 40 and 48°C. The sodium chlorate concentration ranges from 0.63 to 3 M, and sulfuric acid concentration, from 1.7 to 3.5 M. Also listed is the Hammett acidity, $-H_0$ (or $\log(h_0)$), corresponding to each sulfuric acid concentration. The upper temperature of methanol–chlorate experiments was limited to 48°C. At higher temperatures, the time required to scan the sample became significant compared to the half-life of methanol. There are also concerns about loss of methanol by evaporation at higher temperatures. The initial methanol charge in each experiment corresponded to a concentration of approximately 0.032 ± 0.004 M. The mercuric nitrate concentration was 0.016 M in all experiments except two in which it was 0.032 or 0.064 M. In each experiment, the concentrations of chlorate and sulfuric acid were in large excess and essentially constant.

Table 2 lists results of analyses (time-averaged concentrations vs. time) for two of the experiments. Column 1 shows the average time of each concentration measurement. Columns 2 to 4 are areas measured under NMR signals corresponding to the species: formic acid, methanol, and cyclohexane (reference standard). Columns 5 and 6 show the concentrations of methanol and formic acid determined from areas and calibration curves. Column 7 is the ratio of methanol concentration and methanol concentration at $t = 0$. Table 2 shows that some formic acid appeared in the initial concentration measurement of each experiment, because we selected the starting time ($t = 0$) of the experiment one or two minutes after the methanol was added to the sample.

Column 8 shows the sum of methanol and formic acid concentrations. The numbers in this column are relatively constant throughout each experiment, indicating that methanol and formic acid are the only species present, and that there is no measurable conversion of formic acid.

Table 3 and Figure 1 show the results of reaction experiments in which the formic-acid–chlorate reaction was investigated. The reactions were conducted at higher temperatures, 68 and 80°C, and at 3-M chlorate and 3-M sulfuric acid. There is considerable scatter in the data, making it difficult to ascertain whether formic acid reacted at all. However, it is clear from the data in Table 3 and Figure 1 that if formic acid did react, the rate of reaction is insignificant compared to that of the methanol–chlorate reaction rate.

Methanol order

Figures 2 to 4 show that methanol order is 1 in these experiments. Figure 2 shows that the methanol concentration decays exponentially. Figures 3 and 4 show that semilogarithmic graphs of the data are linear. Slopes of lines fitted through the data on semilogarithmic plots are the pseudo-first-order rate coefficients, k', in units of s^{-1}. The values of these coefficients are shown in Table 1, column 8.

Table 2. Kinetic Analysis of Methanol–Chlorate Reaction by NMR Spectrometry

Time s	Areas			C = $[CH_3OH]$ M×10^3	$[HCOOH]$ M×10^3	C/C_0	$[CH_3OH]$ + $[HCOOH]$ M×10^3
	HCOOH	CH_3OH	Ref.				
Experiment 4: 2.5 *M* H_2SO_4, 3 *M chlorate*, 0.032 *M methanol*, 0.016 *M*Hg^{2+}, $T = 21.2°C$							
0	0.6	36.4	21.4	34.2	1.8	1.000	36
117	0.8	34.6	21.0	33.1	2.6	0.967	36
233	1.1	34.4	21.8	31.7	3.5	0.927	35
350	1.6	32.6	20.6	31.7	5.4	0.927	37
467	2.3	32.2	22.0	29.3	7.3	0.858	37
583	2.1	30.6	21.5	28.6	6.7	0.837	35
700	2.4	30.7	21.8	28.3	7.6	0.827	36
817	3.1	29.7	21.8	27.2	9.9	0.797	37
933	3.2	28.2	21.6	26.2	10.2	0.766	36
1,050	3.4	27.8	21.3	26.1	11.1	0.763	37
1,167	3.8	26.2	21.7	24.1	12.1	0.706	36
1,283	3.8	26.4	21.5	24.7	12.2	0.722	37
1,400	4.1	24.9	22.2	22.5	12.9	0.658	35
1,517	4.6	23.7	22.2	21.4	14.2	0.626	36
1,634	5.0	23.7	22.0	21.6	15.6	0.633	37
1,750	5.2	23.1	21.9	21.1	16.4	0.618	38
1,867	5.0	22.6	22.0	20.6	15.7	0.602	36
Experiment 20: 3*M* H_2SO_4, 2.4 *M chlorate*, 0.032 *M methanol*, 0.016 *M* Hg^{2+}, $T = 48°C$							
0	3.4	31.3	26.3	23.9	8.8	1.000	33
117	7.7	17.7	26.1	13.6	20.4	0.568	34
233	10.1	9.7	26.7	7.3	26.2	0.305	33
350	11.3	5.8	25.5	4.6	30.5	0.192	35
467	11.5	3.5	25.6	2.8	31.0	0.116	34
583	12.0	2.2	25.9	1.7	32.0	0.072	34
700	12.6	1.5	26.3	1.2	33.1	0.048	34
817	12.6	1.2	26.2	0.88	33.2	0.037	34
933	12.9	0.4	26.8	0.34	33.1	0.014	33
1050	12.6	0.4	26.6	0.33	32.5	0.014	33

Table 3. Kinetic Analysis of Formic Acid-Chlorate Reaction by NMR Spectrometry

Time Total s	Area HCOOH	Area Ref.	[HCOOH] M × 10^3
Experiment 24: 3 *M* H_2SO_4, 3*M chlorate*, 0.047 *M formic acid*, *T* = 68°C			
103	106.4	122.6	49
370	99.7	110.3	51
637	98.9	109.4	51
903	112.2	123.2	51
1,170	105.1	111.3	53
1,437	96.8	113.1	48
1,703	99.6	113.4	49
1,970	96.4	113.5	48
2,237	90.4	109.6	46
2,503	94.7	116.7	46
2,770	95.5	111.1	48
3,037	93.4	112.2	47
Experiment 29: 3 *M* H_2SO_4, 3*M chlorate*, 0.236 *M formic acid*, *T* = 80°C			
103	407.5	86.2	266
370	377.0	83.8	253
637	384.8	78.3	277
903	428.1	83.7	288
1,170	397.2	88.2	254
1,437	408.8	83.6	275
1,703	402.4	86.9	261
1,970	395.7	86.5	258
2,237	384.8	84.1	258

Reproducibility of results and effect of mercuric ion concentration

One method of estimating error for all twenty-three experiments is to examine the standard deviation of the parameter *k* in Table 1 at each temperature. (The parameter *k* is explained in a later section.) The average value of *k* and standard deviation (in units of s^{-1} M^{-2}) are 0.82 ± 0.15 at 21.2°C, 1.08 ± 0.14 at 24.5°C, 2.19 ± 0.21 at 34°C, 3.51 ± 0.69 at 40°C, 8.04 ± 0.45 at 48°C. The ratios of standard deviation to the average value of *k* (in percentage) are 18%, 13.5%, 9.5%, 19.6%, 5.5%, respectively, at the five temperatures.

In all the experiments (except 22 and 23), mercuric ion concentration was set at half the initial methanol concentration. In all of the experiments the solutions remained colorless, showing no evidence of chlorine dioxide. Based on the series of experiments at 48°C in which mercuric nitrate concentration was varied, it appears that the mercuric ion concentration did not influence the rate of reaction within the limits of experimental error.

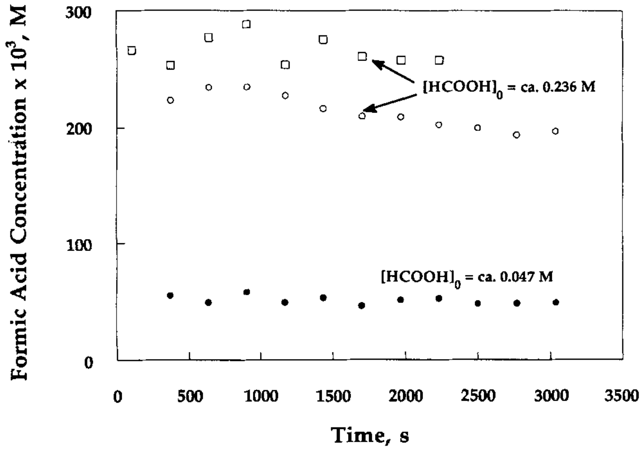

Figure 1. Concentration-time profile in formic acid-chlorate experiments at 80°C.

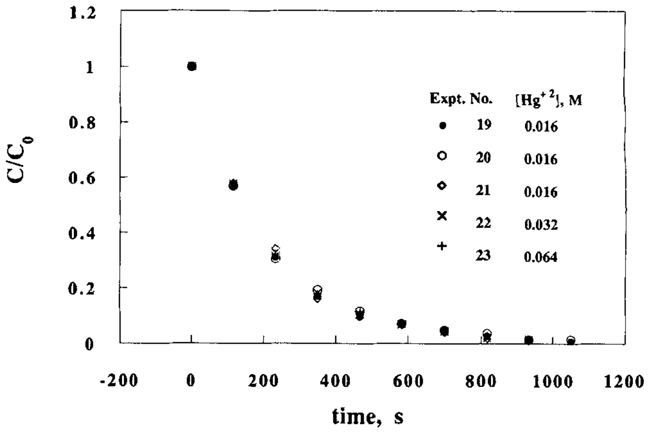

Figure 2. Methanol-time profile at 48°C: effect of concentration of Hg^{+2}.

Determination of kinetic parameters

In Table 1, the values of Hammett acidity were taken from Paul and Long (1957) as listed in Rochester (1970). We found that the following equation accurately correlates the tabulated values of $-H_0$ over a range of 1- to 4.5-M sulfuric acid concentration:

$$-H_0 = -0.373677 + 0.656151 \times [H_2SO_4] - 0.0255295[H_2SO_4]^2. \quad (14)$$

All of the data in Table 1 were analyzed using a multilinear regression program (MINITAB, 1990) to determine kinetic parameters. Hammett acidity, chlorate concentration, temperature, and *k'* were input to the program. The program found the optimal parameters in the logarithmic form of the power law rate equation,

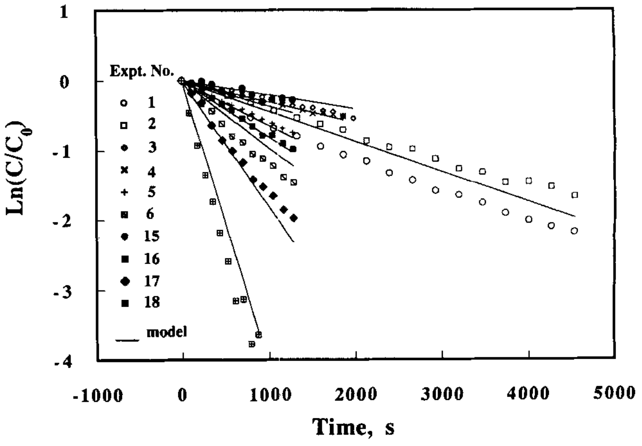

Figure 3. Methanol-time profiles at 21.2 and 40°C: comparison to linear kinetic model.

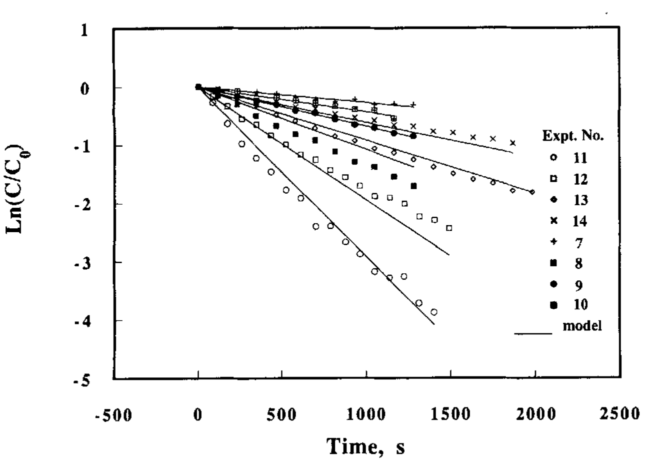

Figure 4. Methanol-time profiles at 24.5 and 34°C: comparison to linear kinetic model.

$$\log(k') = P + Q\log[\mathrm{NaClO_3}] + R\log[h_0] + S(1/T). \quad (15)$$

Table 4 shows the optimal values of the parameters, P, Q, R, and S. It also contains an analysis of variance (ANOVA) table and other statistical parameters. The high R^2 value indicates that the model explains 98.2% of the variability in the data. The goodness of fit is also supported by the low mean square error, indicative of a good model. In addition, the low p values for the coefficients, as well as the regression line, verify that all the parameters are statistically significant. This table shows reaction orders of 1.12 in chlorate and 1.09 in h_0. From the value of $S = -3433$, a value of activation energy, 15,700 cal/mol was calculated.

Reaction orders can also be determined graphically (although not shown here) from sets of data in Table 1. A plot of log (k') vs. log of chlorate concentration for Experiment Numbers 7 to 10 yields a straight line of slope 1.17, corresponding to chlorate order. A plot of log (k') vs. the Hammett acidity function, $-H_0$ (or log (h_0)), for Experiment Numbers 15 to 18 yields a straight line with slope 1.15 corresponding to acid order. These orders agree well with those determined by multilinear regression of all the data.

Table 4. Statistical Parameters for Multilinear Regression

The regression equation is
$\log(k) = 6.40 + 1.12\ \log(\mathrm{NaClO_3}) - 3433\ (1/T) + 1.09^{*}\log(h_0)$
with $R^2 = 98.2\%$.

Predictor	Coef.	Std. Dev.	t-Ratio	p
Constant	6.3958	0.4306	14.85	0.000
Log($\mathrm{ClO_3^-}$)	1.1184	0.09612	11.64	0.000
$1/T$	−3,433.3	131.7	−26.07	0.000
Log(h_0)	1.0878	0.05717	19.03	0.000

Analysis of Variance

Source	DF	SS	MS	F	p
Regression	3	4.6891	1.563	351.21	0.000
Error	19	0.0846	0.0045		
Total	22	4.7736			

Discussion

First-order model

The analysis in the last two sections show that the reaction is essentially first order in methanol and sodium chlorate concentrations and in the Hammett acidity function (within their 95% confidence interval) over the full range of temperatures and concentrations. Assuming the true kinetic order in each component is one, the rate expression is

$$-R_{\mathrm{CH_3OH}} = kh_0[\mathrm{CH_3OH}][\mathrm{ClO_3^-}]. \quad (16)$$

The rate parameter, k, is reported in Table 1, Column 9, and was determined from the experimental pseudo-first-order coefficients, k', in Column 8 as follows:

$$k,\ \mathrm{s^{-1}\cdot M^{-2}} = k'/(h_0[\mathrm{ClO_3^-}]). \quad (17)$$

The Arrhenius parameters for k were determined from the semilogarithmic plot in Figure 5. The final expression for k is

$$k,\ \mathrm{s^{-1}\cdot M^{-2}} = 3.30\times10^{6}\exp(-15{,}658/\mathrm{RT}). \quad (18)$$

Values of k calculated using Eq. 18 are listed in Column 10 of Table 1. This model, Eqs. 16 and 18, reasonably represents the data gathered in each of the experiments, as shown by the solid lines in Figures 3 and 4.

This study suggests that one proton is involved in determining the rate of Eq. 11. Indu (1993) proposed that two protons are involved in determining the overall formation rate of chlorine dioxide. Further study of reactions, Eqs. 12 and 5, at conditions of this study are required to more fully understand the mechanism of this process.

Stoichiometry

The reaction stoichiometry of the methanol-chlorate process depends upon how extensively methanol is oxidized in the stepwise oxidation process, $\mathrm{CH_3OH \rightarrow HCHO \rightarrow HCOOH \rightarrow CO_2}$. The stoichiometric equations associated with these oxidation products are

$$\mathrm{6NaClO_3 + 3CH_3OH + 4H_2SO_4 \rightarrow 6ClO_2 + 3HCHO + 6H_2O + 2Na_3H(SO_4)_2} \quad (19)$$

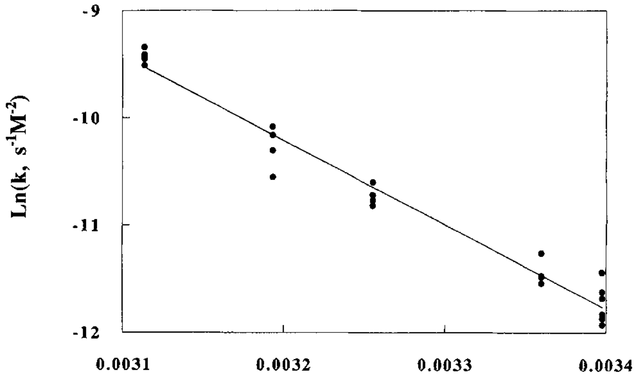

Figure 5. Temperature effect on rate coefficient.

$$12NaClO_3 + 3CH_3OH + 8H_2SO_4 \rightarrow 12ClO_2 + 3HCOOH + 9H_2O + 4Na_3H(SO_4)_2 \quad (20)$$

and

$$6NaClO_3 + CH_3OH + 4H_2SO_4 \rightarrow 6ClO_2 + CO_2 + 5H_2O + 2Na_3H(SO_4)_2 \quad (21)$$

Chlorine dioxide produced per mol of methanol is 2 mol according to Eq. 19, 4 mol according to Eq. 20, and 6 mol according to Eq. 21.

This and previous work show that formaldehye is either absent or in extremely low concentration, and that formic acid is stable and, at least at conditions we have examined, does not react further with chlorate to form carbon dioxide.

Results in this study indicate that the stoichiometry of the methanol–chlorate reaction is represented by Eq. 20. However, results reported in Example 1 of a patent by Norell and Svedin (1990) indicate that one mol of carbon dioxide was produced for about every 3 mol of formic acid. In terms of Eqs. 20 and 21, this by-product mixture corresponds to about 4.5 mol of chlorine dioxide produced per mol of methanol reacted. It appears that stoichiometry may also depend upon factors other than those considered in this study. One of the reasons for this discrepancy may be the addition of sodium chloride to the reaction mixture in the study of Norell and Svedin (1990). The added sodium chloride possibly enhances the production of intermediates (or chlorine) that may, in turn, oxidize some of the formic acid. It was not possible to study the effect of sodium chloride in the present work, because mercuric nitrate would sequester the added chloride.

Use of mercuric salts in studying the methanol–chlorate process

Indu (1993) previously reported that when mercuric nitrate is introduced into a solution of chlorous acid or a solution of both chlorous acid and chlorine dioxide, these components decompose almost instantaneously. (Mercuric nitrate does not cause chlorine dioxide to decompose in the absence of chlorous acid.) It is well known that mercuric ions remove free chloride ions from solutions by forming a soluble complex,

$$Hg^{2+} + 2Cl^- \rightarrow HgCl_2. \quad (22)$$

Ciavatta and Grimaldi (1968) have shown that mercuric chloride exists exclusively as $HgCl_2$ molecules.

It appears from these results that the mercuric ion plays a dual role: (1) a catalyst for the decomposition of chlorous acid and perhaps the decomposition of a complex between chlorous acid and chlorine dioxide; (2) a sequestering agent for removing chloride ions.

In this work, we have studied the methanol–chlorate reaction in the presence of mercuric ions in an NMR tube, scanning the solutions as they react. The mercuric ions prevent the formation of chlorous acid and chlorine dioxide, therefore protecting the NMR instrument from potentially damaging chlorine dioxide gas, and preventing side reactions that might compete with Eq. 11 in consuming methanol, such as reaction with chlorine dioxide.

We are uncertain how mercuric ion participates in the various steps. One scenario is that it prevents chlorous acid from reacting according to Eq. 5 by catalyzing the disproportionation (Kieffer and Gordon, 1968a,b; Hoq et al., 1992a),

$$2HClO_2 \rightarrow HOCl + H^+ + ClO_3^- \quad (23)$$

$$HOCl + HClO_2 \rightarrow Cl^- + 2H^+ + ClO_3^-, \quad (24)$$

and complexing with the chloride product. If this scenario is correct, then the concentration of mercuric ions that would suppress the formation of chlorine dioxide during a kinetics experiment is determined by summing reactions 11, 12, 22, 23 and 24:

$$3CH_3OH + 2HClO_3 + Hg^{2+} \rightarrow 3HCOOH + 3H_2O + HgCl_2 + 2H^+. \quad (25)$$

This equation shows that the minimum mercuric ion concentration required is one-third the initial methanol concentration. Using lower concentrations of mercuric ions would result in accumulation of chlorous acid, formation of chloride ions, and chlorine dioxide. A higher concentration of mercuric ions would remove all the chloride ions.

If formic acid oxides further to carbon dioxide, then for each mole of methanol, a half mole of mercuric ion is required to effectively remove all the chloride ions,

$$2ClO_3^- + 2CH_3OH + Hg^{2+} \rightarrow 2CO_2 + 4H_2O + HgCl_2. \quad (26)$$

Application

Typical operating conditions for one type of commercial reactor are 70°C, 160-mm Hg total pressure, 3-M sodium chlorate, 3-M sulfuric acid, and 3.4-M sodium sulfate. The acidity function, h_-, at these conditions is 12.3. A typical plant producing 20 ton/d (186 mol/min) of chlorine dioxide, has a reactor liquid volume of 25,000 L. This rate would require a methanol conversion rate of 46.5 mol/min, or 0.00186 M/min, assuming the stoichiometry shown by Eq. 20.

We could test the hypothesis that the methanol–chlorate reaction rate, Eq. 11, is an important step in chlorine dioxide production by comparing the rate of this step with the methanol conversion rate required to produce chlorine dioxide at the preceding commercial conditions. There is one difficulty with this approach—the methanol content of a commercial reactor solution is not monitored because there is no convenient way to measure organics in these very reactive solutions at the plant site. The methanol concentration is needed to predict the rate of Eq. 11 using Eqs. 16 and 18.

In a roundabout way, this difficulty may be overcome by assuming that the rate expression, Eq. 13, is a representative model of chlorine dioxide rate in a commercial system. Then this equation can be used to estimate the methanol concentration in a commercial reactor by inserting the preceding set of concentrations and rate. This calculation yields a methanol concentration of 0.012–0.013 M. At this concentration and the conditions just given, the rate of methanol consumption predicted by Eqs. 16 and 18 is about 0.01 M/min, or 5–6 times that required to produce chlorine dioxide in the commercial system. Although the results of this comparison do not agree, they are within an order of magnitude of each other. The difference may reflect errors due to extrapolation of the two models, Eq. 13 and Eqs. 16 and 18, to commercial conditions. (Note that there is no published Hammett acidity scale for sulfuric acid–sodium sulfate mixtures. To make the preceding comparison, the value of h_0, used in Eq. 16, was estimated to be 12.5. The estimate is based on the following reasoning. At 3-M sodium chlorate, in the absence of sodium sulfate, the values of h_- and h_0 are about the same in the acid concentration range of 2.5- to 3.5-M H_2SO_4. Also with this range, when 3.4-M sodium sulfate is in solution, the h_- function drops to about 54% of its value in the absence of sodium sulfate. We assumed that sodium sulfate has the same effect on the Hammett function.)

Conclusions

We have measured the rate of reaction of methanol with chlorate ions in acid solution in the absence of chlorous acid and chlorine dioxide formation. We have shown that this reaction is first order in methanol and chlorate concentrations and in the Hammett acidity function. Based on these results and previous results showing that chlorous acid and formaldehyde are intermediate species, it is likely that the direct reaction of methanol and chlorate in acidic solution is an important step in the production of chlorine dioxide. At the conditions of this work, no formaldehyde was observed, and formic acid formed at the rate that methanol reacted, reinforcing the conclusion from our earlier qualitative work that formaldehyde reacted rapidly, presumably with chlorate. Formic acid was stable and did not react with chlorate at a measurable rate even at concentrations and temperatures representative of a commercial process.

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Notation

h_-, H_- = acidity function for sulfuric acid and sodium sulfate solutions (where $H_- = -\log_{10}(h_-)$ (Indu et al., 1991b); $-H_- = -2.32 + 2.64a + 0.219b - 1.16a^2 - 0.016b^2 + 0.44ab + 0.12c$, where $a = [H_2SO_4]/b$; $b = [H_2SO_4] + [Na_2SO_4]$; and $c = [NaClO_3]$

R_{CH_3OH} = methanol reaction rate, M^*s^{-1}.

T = temperature, K

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Appendix

NMR equipment and procedures

Proton NMR spectra were measured using a 5-mm broadband switchable probe in a Varian XL-400 Fourier transform spectrometer operating at 399.915 MHz. The large water signal was suppressed by selective saturation during a 20-s delay prior to acquisition. In these experiments, cyclohexane in carbon tetrachloride was used as an external reference standard. A 1% v/v solution of cyclohexane in carbon tetrachloride was placed inside a capillary tube inserted coaxially into the 5-mm NMR tube containing the solution. The cyclohexane signal was set at 1.38 ppm with reference to tetramethylsilane (TMS).

Relaxation times of the various chemical components in reaction solutions were determined by standard T_1 inversion recovery experiments, using a 90° pulse width of 33.7 μs. The relaxation time for formic acid was 10.27 s; for methanol, 6.97 ± 0.2 s; and for cyclohexane, 4.65 ± 0.09 s. Relaxation time for **$HCOOCH_3$** and $HCOOCH_3$ were found to be 13.27 ± 1.85 and 8.22 ± 0.84 s; however, since we did not observe methyl formate, the longest relaxation time for the reaction solutions was taken to be 10 s, corresponding to formic acid.

During the early stage of this work, we conducted several preliminary experiments using a pulse width of 15° and pulse repetition period of 5 s. Data from these experiments were not reproducible and did not yield exponential curves for C/C_0 vs. time. We suspect that these conditions may not be suitable for studying a transient system. In the experiments listed in this work, we made use of the recommendations in recent literature for improving NMR analyses (Traficante, 1992; Traficante and Steward, 1994). These articles showed that a 74° tip angle, and a pulse repetition period (PR) to relaxation time ratio (PR/T1) of 2, yield 90% integral accuracy. Using (PR/T1) of 2 provides adequate time for nuclei to relax to their original positions between scans. A pulse width of 29 μs and a pulse repetition period of 20 s were used in all experiments. This set of parameters yields a signal-to-noise ratio that is 30% higher than that of a previously accepted procedure called the 90°- wait 5T1 method (Traficante and Steward, 1994). Signal-to-noise ratio is proportional to the square root of the number of scans of each sample (Traficante, 1991).

Temperature measurement

The NMR console monitors the temperature outside the sample tube. The temperature of a solution with the tube was determined indirectly using a solution of ethylene glycol sealed in a sample tube, since the distance between two NMR signals for ethylene glycol is temperature dependent. We made use of this principle to estimate the time it takes a reaction solution to reach constant temperature in the NMR spectrometer. In a typical experiment, ethylene glycol in the sealed tube was first heated in the instrument for sufficient time to reach a constant temperature. The sample was then removed from the instrument for 30 s (to simulate one of the initial steps in the kinetics experiment), reinserted into the instrument, and scanned at regular intervals of 15 s. Temperature was calculated from the distance between the two signals. A temperature–time graph is shown in Figure 6 for a controlled instrument temperature of 48°C. The sample reached 95% of the final value of the temperature in just over 100 s. This experiment was repeated to determine heat-up times at other final temperatures.

Time-averaged FT-NMR data

A kinetics experiment involves measuring the concentration of a reacting species (in this case, methanol) at several different times. Each concentration measurement involves scanning the sample four times in order to accumulate sufficient information to assure good accuracy and sensitivity. Information from these scans is analyzed by the instrument, and a time-averaged signal recorded. The signal can be converted to concentration by calibrating the instrument. In kinetic experiments, the concentration of reacting species changes with time. If the time required to complete the multiple-scanning process is Δt (in this work, 88 s), the concentration determined from the signal is not the true concentration at time, t, but rather a time-averaged concentration. If Δt is significant compared to the half-life of the species, the difference between the true concentration at t and the time-averaged value will be great.

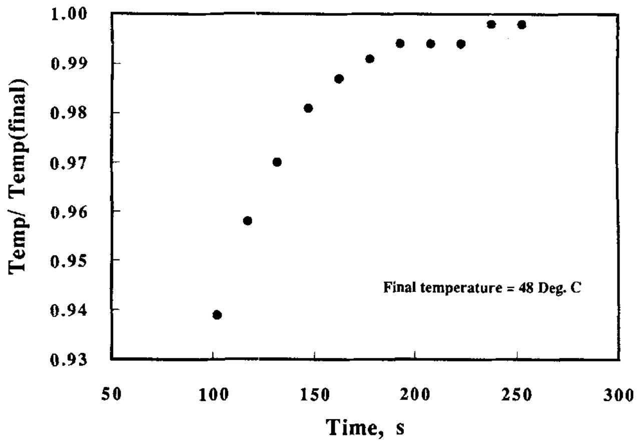

Figure 6. Temperature response in ethylene glycol probe: final temperature = 48°C.

The time-averaged concentration vs. time data can be analyzed to determine rate parameters if the reaction follows first-order kinetics. For other orders, the interpretation of the data is more difficult and subject to error.

For a first-order reaction, the reacting species concentration, C, depends upon time according to the expression

$$C = C_0 \exp(-k't) \qquad (1')$$

where k' is the rate coefficient. In a typical experiment, a sample is scanned repeatedly over a time period from t to $t + \Delta t$, and the time-averaged concentration $|C|$ is recorded. The average concentration is related to the instantaneous concentration by the expression,

$$|C| = (1/\Delta t) \int C dt \qquad (2')$$

$$= (C_0/\Delta t) \int \exp(-k't)\, dt, \qquad (3)$$

where the integration limits are t to $t + \Delta t$.

The integrated solution to Eq. 3′ is

$$|C| = \{(C_0/k'\Delta t)[1 - \exp(-k'\Delta t)]\} \exp(-k't). \qquad (4')$$

If Δt is the same each time the concentration is measured, the term in brackets {} will be a constant throughout the experiment. A plot of ln ($|C|$) vs. t yields a straight line with a slope equaling the true rate coefficient, k'.

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