

# Methanol-Formic Acid Esterification Equilibrium in Sulfuric Acid Solutions: Influence of Sodium Salts

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Molar equilibrium quotients of methanol-formic acid esterification were measured in the concentration range 0–5 M sulfuric acid in the presence and absence of sodium sulfate and sodium nitrate. The sulfuric acid and sodium salts shift equilibrium in favor of methyl formate. Sulfuric acid appears to catalyze the rate at which the system approaches equilibrium. Temperature had no measureable influence on the measured quotients. All of the data measured at 25 °C were correlated with an expression of the form  $\ln(K_e) = A + B[H_2SO_4] + C[Na_2SO_4] + D[NaNO_3]$  with reasonable accuracy. This expression has application in modeling of reactors in commercial chlorine dioxide processes that are based on methanol-chlorate chemistry.

## Introduction

Chlorine dioxide is produced industrially by reacting methanol with sodium chlorate in aqueous sulfuric acid solutions. The reaction produces formic acid as an intermediate.<sup>1,2</sup> It reacts with methanol, producing methyl formate which volatilizes, contaminating the gas-phase chlorine dioxide product. Before one can estimate the rate at which methyl formate enters the gas phase, one must be able to estimate the equilibrium liquid-phase concentration of methyl formate at industrial conditions, typically at methanol and formic acid concentration below 0.5 M, and sodium chlorate, sodium sulfate and sulfuric acid concentrations up to 3, 2.5, and 4 M, respectively.

Esterification reactions,



and the reverse reactions, hydrolysis of carboxylic esters, have been the subject of intensive kinetic and mechanistic studies during the past century. Berthelot et al.<sup>3–5</sup> investigated esterification of acetic acid and hydrolysis of ethyl acetate. Numerous workers have studied the kinetics of these reactions and are cited in texts and review articles.<sup>6–9</sup> These works found that ester hydrolysis is catalyzed by hydrogen and hydroxylic ions. Several articles discuss the methanol-formic acid-methyl formate system.<sup>10–18</sup> While many of these studies were conducted in the absence of water, or at low concentrations of water, a few were conducted with dilute concentrations of organics, and are more closely related to this work. None of the previous works describe the effect of sulfuric acid on the equilibrium.

Concentration equilibrium quotients of most esterification reactions,

$$K_e = \frac{[RCOOR'][H_2O]}{[R'OH][RCOOH]} \quad (2)$$

have small or negligible temperature dependence. Gladii et al.,<sup>14</sup> for example, reported an enthalpy change of about 4 kJ/mol for methyl formate hydrolysis; Williams et al.<sup>15</sup> found no temperature effect. Many workers used mineral acids as catalysts, presumably to decrease the time to equilibrium of their solutions. The acid not only catalyzes the reaction, it causes a variation in  $K_e$  values. Trimble

and Richardson<sup>16</sup> showed that  $K_e$  increases linearly with perchloric acid concentration for the acetic acid-ethyl alcohol reaction. They reasoned that the acid changes the activity coefficients of reacting species. Euler<sup>17</sup> studied the hydrolysis equilibrium at 50 °C of methyl formate, using hydrochloric acid as a catalyst. Schultz<sup>18</sup> reported that the equilibrium quotient of hydrolysis (equivalent to  $K_e^{-1}$  in this study) decreases linearly with hydrochloric acid concentration.

Schultz<sup>18</sup> and others also found that the equilibrium quotient depends upon the composition of the solutions, in particular, the relative amounts of water and organic species in solution. He conducted two experiments at dilute methyl formate concentration which are within the range of interest of the present study. He found values of  $K_e = 4.3$  and 4.1. Gladii et al.<sup>14</sup> also studied hydrolysis experiments over a wide range of relative concentrations of water and methyl formate. They correlated results in terms of "initial" methyl formate mole fraction,  $X_0$ , and temperature, using the expression,

$$\ln(K_e) = 3.112 + 0.0039X_0 - (0.0051 - 0.85 \times 10^{-5}X_0)T \quad (3)$$

For dilute solutions and 25 °C, the terms containing  $X_0$  are negligible and eq 3 predicts  $K_e = 4.9$ . No results have been reported for the equilibrium quotient in the presence of sulfuric acid and sodium salts.

## Experimental Section

Methanol and formic acid, each at 0.5 M (or in a few experiments 1.0 M), were combined with D<sub>2</sub>O or sulfuric acid-D<sub>2</sub>O solutions ranging in concentration from 0 to 5 M. The solutions were maintained at constant temperature for various lengths of time and analyzed by proton NMR spectroscopy. Alternatively, 0.5 M methyl formate was combined with sulfuric acid, and the equilibrium approached from the reverse direction. For the samples containing salts, appropriate amounts of salts were dissolved in acid solution within the NMR tube and volumes adjusted to 1 mL.

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. To ensure good signal to noise ratio and sufficient relaxation time, multiple scans (generally 8 or 16) were obtained using a pulse angle of 15° and a 12-s pulse cycle. The large water signal was suppressed by selective saturation during a 10-s delay time prior to acquisition.

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Table I. Equilibrium Data and Results at 25 °C: Influence of Sulfuric Acid

time	[H <sub>2</sub> SO <sub>4</sub> ], M	[HCOOCH <sub>3</sub> ], M	[CH <sub>3</sub> OH], M	[HCOOH], M	[H <sub>2</sub> O], M	K <sub>e</sub> (exptl)	std dev	K <sub>e</sub> (calcd)
30 min	0.0	0.0000	0.500	0.500	53.3			
3 days	0.0	0.0360	0.964	0.464	52.3	4.2		
3 days	0.0	0.0176	0.482	0.482	53.3	4.1		
3 days	0.0	0.0159	0.484	0.484	52.3	3.6		
3 days	0.0	0.0423	0.458	0.958	52.3	5.0		
3 days	0.0	0.0356	0.964	0.464	52.3	4.2		
3 days	0.0	0.0395	0.461	0.961	52.3	4.7		
						4.3	0.51	4.0
15 min	0.5	0.0188	0.481	0.481	52.3	4.2		
3 days	0.5	0.0194	0.481	0.481	52.3	4.4		
15 min	0.5	0.0195	0.481	0.481	52.3	4.4		
3 days	0.5	0.0452	0.455	0.955	51.2	5.3		
3 days	0.5	0.0426	0.957	0.457	51.2	5.0		
3 days	0.5	0.0436	0.456	0.956	51.2	5.1		
						4.7	0.46	4.5
3 days	1.0	0.0195	0.481	0.481	51.2	4.3		
15 min	1.0	0.0232	0.477	0.477	51.2	5.3		
3 days	1.0	0.0239	0.476	0.476	51.2	5.4		
3 days	1.0	0.0365	0.964	0.464	50.2	4.1		
3 days	1.0	0.0225	0.477	0.477	51.2	5.1		
3 days	1.0	0.0497	0.450	0.950	50.2	5.8		
3 days	1.0	0.0411	0.959	0.459	50.2	4.7		
3 days	1.0	0.0474	0.453	0.953	50.2	5.5		
3 days	1.0	0.0245	0.476	0.476	51.2	5.5		
						5.1	0.59	5.1
3 days	1.5	0.0468	0.953	0.453	49.1	5.3		
3 days	1.5	0.0521	0.948	0.448	49.1	6.0		
3 days	1.5	0.0493	0.951	0.451	49.1	5.7		
3 days	1.5	0.0510	0.949	0.449	49.1	5.9		
3 days	1.5	0.0266	0.473	0.473	50.1	5.9		
3 days	1.5	0.0300	0.470	0.470	50.1	6.8		
3 days	1.5	0.0532	0.447	0.947	49.1	6.2		
						6.0	0.46	5.8
15 min	2.0	0.0275	0.973	0.473	49.0	6.0		
3 days	2.0	0.0287	0.971	0.471	49.0	6.3		
3 days	2.0	0.0553	0.945	0.445	48.0	6.3		
3 days	2.0	0.0526	0.447	0.947	48.0	6.0		
3 days	2.0	0.0285	0.471	0.471	49.0	6.3		
3 days	2.0	0.0293	0.471	0.471	49.0	6.5		
						6.2	0.20	6.6
3 days	2.5	0.0338	0.466	0.466	47.9	7.5		
3 days	2.5	0.0348	0.465	0.465	47.9	7.7		
						7.6	0.18	7.5
15 min <sup>a</sup>	3.0	0.0371	0.463	0.463	46.9	8.1		
15 min	3.0	0.0382	0.462	0.462	46.9	8.4		
15 min	3.0	0.0379	0.462	0.462	46.9	8.3		
15 min	3.0	0.0363	0.464	0.464	46.9	7.9		
15 min	3.0	0.0693	0.431	0.431	46.9	8.1		
15 min	3.0	0.0740	0.926	0.426	45.9	8.6		
15 min	3.0	0.0397	0.460	0.460	46.9	8.8		
						8.3	0.30	8.6
3 days	3.5	0.0440	0.456	0.456	45.6	9.7		
3 days	3.5	0.0440	0.456	0.456	45.6	9.6		
3 days	3.5	0.0840	0.416	0.916	44.6	9.8		
						9.7	0.11	9.7
15 min	4.0	0.0463	0.454	0.454	44.4	10.0		
3 days	4.0	0.0481	0.452	0.452	44.4	10.5		
3 days	4.0	0.0468	0.453	0.453	44.4	10.1		
3 days	4.0	0.0936	0.406	0.906	43.4	11.0		
3 days	4.0	0.0901	0.910	0.410	43.4	10.5		
3 days	4.0	0.0495	0.451	0.451	44.4	10.8		
						10.5	0.39	11.1
6 h	5.0	0.0633	0.437	0.437	42.0	13.9		
6 h	5.0	0.0622	0.438	0.438	42.0	13.6		
						13.8	0.21	14.3

<sup>a</sup> Equilibrium was established starting with 0.5 M HCOOCH<sub>3</sub> in 3 M H<sub>2</sub>SO<sub>4</sub>.

In these experiments, cyclohexane in carbon tetrachloride was used as a reference standard. A 10% v/v solution of cyclohexane in carbon tetrachloride was placed inside a capillary tube inserted coaxially into the 5-mm NMR tube. The cyclohexane signal was set at 1.38 ppm with reference to tetramethylsilane.

In order to obtain accurate quantitative measure of the signal areas, we used a relaxation delay of at least 4 or 5

times the relaxation time of the compound in the mixture with the greatest relaxation time. Relaxation times of different compounds were determined by standard inversion recovery experiments, using a 90° pulse width of 33.7 μs. 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<sub>3</sub> was 13.27 ± 1.85 s, while for methyl protons it was 8.22 ± 0.84 s. We concluded, for

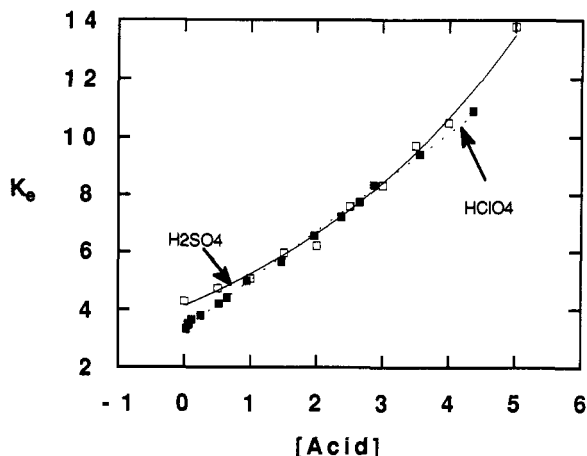


Figure 1. Effect of acid concentration on esterification equilibrium quotients. Open symbols, this work; solid symbols, ref 16.

a pulse width of 33.7, a relaxation delay of  $13.27 \times 4 = 53.08$  s was sufficient. A relaxation delay of 10 s was used with a pulse width of 5  $\mu$ s (equivalent to approximately 15°).

## Results and Discussion

**Effect of Sulfuric Acid.** A typical NMR spectrum of an equilibrated sample shows a signal corresponding to protons of cyclohexane (reference) at 1.38 ppm, the proton attached to carbon in formic acid at 8.0 ppm, and methyl protons of methanol at 3.0 ppm. Signals corresponding to methyl formate protons attached to the carbonyl carbon and the methyl group appear at 7.9 and 3.4 ppm, respectively. These signal positions have been reported before.<sup>19</sup>

Because methyl formate begins reacting immediately when added to sulfuric acid, we were unable to prepare standard methyl formate-sulfuric acid solutions for calibrating the NMR. Furthermore, we observed that the slopes of calibration curves (concentration versus signal area) for methanol and formic acid depend on sulfuric acid concentration.

In determining species concentrations in the equilibrated solutions, we assumed that the slopes of calibration curves for methanol and methyl formate, based on areas under signals for methyl protons, are identical. Since we knew the initial concentration of all solutions accurately, we determined equilibrium concentrations from two area measurements ( $A_{CH_3OH}$ , the area under the 3.0 ppm signal, and  $A_{HCOOCH_3}$ , the area under the 3.4 ppm signal) and the initial species concentrations.

$$[HCOOCH_3] =$$

$$\{A_{HCOOCH_3} / (A_{HCOOCH_3} + A_{CH_3OH})\} [CH_3OH]_{\text{initial}} \quad (4)$$

$$[CH_3OH] = [CH_3OH]_{\text{initial}} - [HCOOCH_3] \quad (5)$$

$$[HCOOH] = [HCOOH]_{\text{initial}} - [HCOOCH_3] \quad (6)$$

Table I shows the values of equilibrium quotients which were calculated from concentrations determined in the above manner at various sulfuric acid concentrations and at 25 °C. In the absence of sulfuric acid (see the first entry in Table I), methyl formate was not detected at 30 min in a solution of 0.5 M methanol and 0.5 M formic acid. This solution was reexamined again at 3 days and again at 3 weeks (not shown). The calculated equilibrium quotients did not change over this period. We concluded therefore that 3 days was sufficient time to achieve equilibrium for a sample containing no sulfuric acid. We

determined an average equilibrium quotient of 4.3. By comparison, Schultz<sup>18</sup> reported a value of 4.1, Gladii et al.<sup>14</sup> a value of 4.9, and Euler<sup>17</sup> a value of 5.0. Williams et al.<sup>15</sup> reported a value of 4.1 at 100 °C.

For samples containing sulfuric acid, 15 min was sufficient time to achieve equilibrium, although some samples were left to equilibrate for much longer periods. The reproducibility of measured  $K_e$  values was reasonably good, as shown by the values of standard deviation of each series in Table I. Also, changing the initial concentration conditions did not influence the resulting equilibrium quotient (starting with methanol or formic acid concentration at 1.0 M or approaching equilibrium from the opposite direction, starting with a solution containing only methyl formate). If each standard deviation ( $\times 100$ ) is divided by the corresponding equilibrium quotient, the average of the resulting values for the entire data set is 5.4%.

Increasing the sulfuric acid concentration between 0 and 5 M increased the equilibrium quotient by more than a factor of 3, as shown in Figure 1 and Table I. The data could be represented reasonably accurately by the exponential expression

$$K_e = 4 \exp\{(1/4)[H_2SO_4]\} \quad (7)$$

as shown by the solid line in Figure 1. By comparison, Trimble and Richardson<sup>16</sup> reported equilibrium quotients for a different, but analogous, system, the esterification of acetic acid with ethyl alcohol in perchloric acid solutions. Their data are also plotted in Figure 1. The values of these quotients are within the same order of magnitude as those corresponding to the sulfuric acid solutions; however, the quotients of Trimble and Richardson exhibit a linear trend with acid concentration.

Table II shows that equilibrium quotients were reasonably independent of temperature, at least within the normal variation of the data. These results are in general agreement with previous works.<sup>14,15</sup>

**Effect of Sodium Sulfate and Sodium Nitrate.** Table III shows equilibrium quotients for sulfuric acid solutions containing either sodium sulfate or sodium nitrate, or both salts. Instead of showing all of the data of each experiment, we show the average equilibrium quotient determined at each concentration condition, the total number of repetitions, and the standard deviation at each condition.

These salts each increased the equilibrium quotients, although to a lesser extent than sulfuric acid. Also, in contrast to sulfuric acid alone, neither of the salts significantly enhanced the rate at which the system approached equilibrium.

Sodium nitrate was used in this study as a model for sodium chlorate, which is a component in commercial chlorine dioxide production. Sodium chlorate could not be studied, because it reacts vigorously with methanol, producing chlorine dioxide under acidic conditions. Other workers<sup>20</sup> have shown that while sodium ions effectively increase the acidity of sulfuric acid solutions by water abstraction, nitrate and chlorate ions do not affect acidity. Therefore, by substituting sodium nitrate for sodium chlorate in this study, we have not changed the solution acidity. What we do not know from this study, however, is whether chlorate or nitrate ions exhibit any other influence on the system which would change the value of the equilibrium quotient, or whether nitrate and chlorate have equivalent or different influences on the quotient.

For fitting all of the data of this study, we used the logarithmic form of eq 7 to express the influence of each

Table II. Equilibrium Results versus Temperature

temp, °C	[H <sub>2</sub> SO <sub>4</sub> ], M	[HCOOCH <sub>3</sub> ], M	[CH <sub>3</sub> OH], M	[HCOOH], M	[H <sub>2</sub> O], M	<i>K<sub>e</sub></i> (exptl)	std dev
35	3.0	0.0410	0.459	0.459	46.9	9.2	
45	3.0	0.0396	0.460	0.460	46.9	8.6	
55	3.0	0.0379	0.462	0.462	46.9	8.3	
65	3.0	0.0398	0.460	0.460	46.9	8.6	
						8.7	0.36

Table III. Equilibrium Data and Results at 25 °C: Influence of Sodium Salts

time	[Na <sub>2</sub> SO <sub>4</sub> ], M	[H <sub>2</sub> SO <sub>4</sub> ], M	[NaNO <sub>3</sub> ], M	no. of expt	<i>K<sub>e</sub></i> (exptl)	std dev	<i>K<sub>e</sub></i> (calcd)
2 days	0.0	0.0	2.0	1	4.3		4.9
2 days	0.0	0.0	4.0	3	6.5	0.42	6.2
2 days	0.0	0.0	6.0	3	7.6	0.19	7.6
2 days	0.0	0.0	8.0	2	9.8	0.36	9.5
4 days	0.0	2.0	1.0	3	7.6	0.12	7.4
4 days	0.0	2.0	2.0	3	8.4	0.38	8.3
4 days	0.0	2.0	3.0	2	9.1	0.50	9.2
4 days	1.6	2.0	2.0	3	8.7	0.29	9.1
3 days	0.8	1.0	0.0	3	5.4	0.34	5.4
3 days	0.8	2.0	0.0	4	7.3	0.17	7.0
3 days	0.8	3.0	0.0	4	9.3	0.15	9.0
3 days	0.8	4.0	0.0	6	12.1	0.37	11.6
3 days	1.6	1.0	0.0	3	5.2	0.13	5.7
3 days	1.6	2.0	0.0	3	7.6	0.23	7.3
3 days	1.6	3.0	0.0	3	9.6	0.27	9.4
3 days	1.6	4.0	0.0	3	12.4	0.29	12.2
3 days	2.4	1.0	0.0	3	5.2	0.93	5.9
3 days	2.4	2.0	0.0	3	8.4	0.20	7.7
3 days	2.4	3.0	0.0	3	10.6	0.24	9.9
3 days	2.4	4.0	0.0	2	12.7	1.11	12.8
3 days	0.0	1.0	1.5	3	6.4	0.38	6.1
3 days	0.0	1.0	3.0	3	7.3	0.29	7.1
3 days	1.6	1.0	1.5	4	7.0	0.14	6.7
3 days	1.6	1.0	3.0	3	7.5	0.27	7.8

Table IV. Results of Multilinear Regression: Results for Eq 8

param	param value	std dev	<i>t</i> ratio
<i>A</i>	1.38	0.02	59.0
<i>B</i>	0.256	0.008	31.0
<i>C</i>	0.060	0.01	5.5
<i>D</i>	0.109	0.006	18.0

no. of data points used  
coeff of regression

34  
0.971

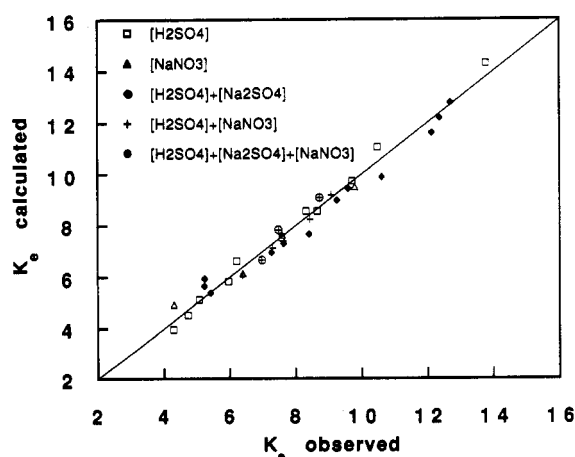


Figure 2. Comparison of measured equilibrium quotients and predictions of eq 8 with parameters in Table IV.

component on the equilibrium quotient and assumed that contributions of all components were additive within the range of the experimental conditions. We fit all data in Tables I and III to

$$\ln(K_e) = A + B[\text{H}_2\text{SO}_4] + C[\text{Na}_2\text{SO}_4] + D[\text{NaNO}_3] \quad (8)$$

using a multilinear regression/statistical analysis program

entitled MINITAB.<sup>21</sup> In the analysis, the program finds the values of the parameters, *A*, *B*, *C*, and *D*, which minimize the difference between experimental and calculated values of  $\ln(K_e)$  and performs a statistical analysis of the parameters. Table IV shows values and standard deviations of each of the adjustable parameters in this equation. Also included in Table IV are results of a Student's *t* test of the data. A reasonably good fit was obtained as shown by the large *t* ratios for each parameter and the adjusted coefficient of determination near unity (i.e.,  $R^2 = 0.971$ ).

Tables I and III (last column) show values of equilibrium quotients for each data set calculated using eq 8. Figure 2 shows a plot of calculated versus experimental values. Equation 8, an empirical expression, has potential value as a predictive expression which can be incorporated into a general process model of a commercial chlorine dioxide process based on methanol-chlorate chemistry.

## Conclusions

Molar equilibrium quotients of methanol-formic acid esterification were measured in the concentration range 0–5 M sulfuric acid, and in the temperature range, 25–65 °C, using <sup>1</sup>H NMR spectroscopy. Equilibrium shifts in favor of methyl formate as sulfuric acid concentration increases and is not dependent upon temperature. The presence of sulfuric acid greatly reduces the time required to achieve equilibrium. Sodium sulfate and sodium nitrate shift the equilibrium toward methyl formate, but to a lesser extent than sulfuric acid. These sodium salts do not exhibit the strong catalytic effect shown by sulfuric acid.

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