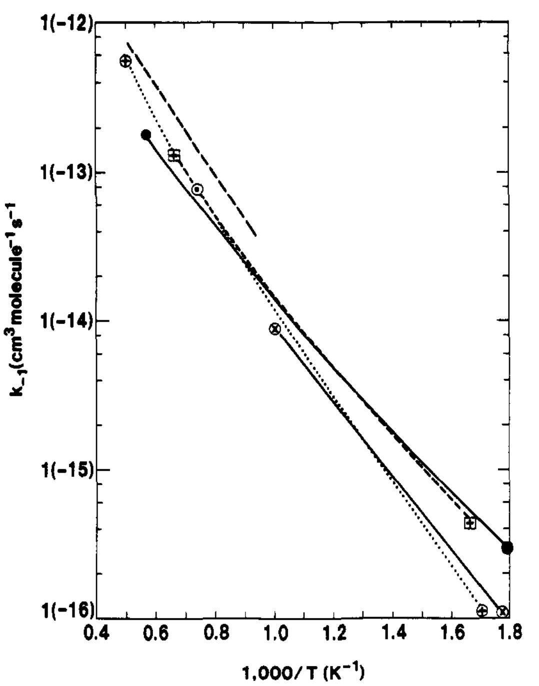

Figure 6. Comparison of $k_{-1}(T)$ data. (●—●) this study; (---) Möller et al.;[10] (⊙) Clarke and Dove;[9] (⊗—⊗) Allara and Shaw;[13b] (⊕···⊕) Schatz et al.;[30] (⊞---⊞) Truhlar and co-workers[32] (J2A).

general temperature dependence. Interestingly, the value for k_{-1} reported by Clark and Dove[9] at 1340 K (7.6×10^{-14} cm^3 molecule^{-1} s^{-1}) is in reasonably good agreement (see Figure 6) with the value calculated by using expression VIII at the same temperature (5.9×10^{-14} cm^3 molecule^{-1} s^{-1}). The expression for $k_{-1}(T)$ recommended by Allara and Shaw[13b] is also shown in Figure 6. The data used to derive this expression were derived primarily from low-temperature experiments (300 K $\leq T \leq$ 700 K) and thus there is a lack of curvature. Of more interest and import, however, is the rather large discrepancy between this evaluated expression and the values derived from eq X and those reported by Truhlar and co-workers.[32] Assuming that the equilibrium constant K_1 is well established, either our derived values (eq X) and Truhlar's calculated ones are in error or there is a problem with the low-temperature measurements of k_{-1} as evaluated by Allara and Shaw.[13b,33]

In conclusion, we have reported rate constants for reaction 1 that were derived from experimental H-atom decays obtained under kinetically isolated conditions. The calculated rate constants of Truhlar and co-workers[32] are in excellent agreement with these experimental results. However, our $k_1(T)$ data are not in agreement with those of Roth and Just[5] or with those recommended by Warnatz[1] (the present results are smaller at 1700 K by about a factor of 3.5). In addition, we report a discrepancy with previous determinations of $k_{-1}(T)$[13b] and with the recommended value for the (low pressure) thermal decomposition rate constant of methane.[1] In order to resolve these disagreements, further kinetic studies on reactions 1, −1, and 3 are indicated.

Acknowledgment. We thank two referees for pointing out the potential kinetic complication associated with singlet methylene. We also acknowledge the contributions of Dr. W. Tao and Mr. J. Quartemont in the computer simulations. This work was supported by the Division of Chemical Sciences, U.S. Department of Energy, Washington, DC, under Contract No. DE-AC02-76CH00016.

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[33] It is interesting to note that an expression for $k_{-1}(T)$ derived from the $k_1(T)$ evaluation of Shaw[13a] (via $k_{-1} = k_1/K_1$) is in better agreement with eq X and the calculated values of Truhlar and co-workers[32] than it is with the $k_{-1}(T)$ expression recommended by Allara and Shaw.[13b]

Kinetics of the Reaction of Chlorine with Formic Acid in Aqueous Sulfuric Acid

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(Received: December 12, 1989; In Final Form: July 26, 1990)

In sulfuric acid solution, the rate of reaction of chlorine with formic acid is proportional to formic acid and chlorine concentrations and is inversely proportional to the acidity function h_-. The kinetic parameters are nearly identical with those for the reduction of bromine to bromide ions by formic acid. The two reactions appear to follow similar mechanisms—equilibrium ionization of formic acid followed by direct reaction of a formate ion with a halogen molecule.

Introduction

The oxidation of formic acid by chlorine in sulfuric acid solution may be an important reaction in the commercial production of chlorine dioxide based on the methanol–chlorate process.[1-3] Kinetic information on this reaction has not been reported.

Previous work[4] on the bromine–formic acid reaction has demonstrated that the stoichiometry involves equilibrium ionization of formic acid

$$HCOOH \rightleftharpoons HCO_2^- + H^+ \qquad (1)$$

and the bromine–formate reaction

$$Br_2 + HCO_2^- \rightarrow H^+ + 2Br^- + CO_2 \qquad (2)$$

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[1] Masschelein, W. J. *Chlorine Dioxide*; Ann Arbor Science: Ann Arbor, MI, 1979.

[2] Norell, M. U.S. Patent No. 4,770,868, Sept 13, 1988.

[3] Swindells, R.; Fredette, M. C. J. U.S. Patent No. 4,325,934, Apr 20, 1982.

[4] Hammick, D. L.; Hutchison, W. K.; Snell, F. R. *J. Chem. Soc.* **1925**, *127*, 2715.

0022-3654/91/2095-0681$02.50/0

Others[5] have used this known stoichiometry to construct an H_- acidity scale for formic acid ionization in nitric, perchloric and sulfuric acids. The rate law for this system can be written

$$-\frac{d[Br_2]}{dt} = k'K_a \frac{\gamma_{HCOOH}[HCOOH][Br_2]}{\gamma_{HCO_2^-}\gamma_{H^+}[H^+]} \qquad (3)$$

where K_a is the ionization constant for formic acid, k' is the rate coefficient for the bromine–formate reaction in terms of bromine disappearance, and γ's are molar activity coefficients. The acidity scale is defined by

$$H_- = -\log h_- \qquad (4)$$

where

$$h_- = \frac{[H^+]\gamma_{H^+}\gamma_{HCO_2^-}}{\gamma_{HCOOH}} \qquad (5)$$

It is reasonable to expect that the chlorine–formic acid reaction may have a rate law analogous to eq 3. This work is an experimental study of the kinetics of this reaction in sulfuric acid solution.

Experimental Section

The equipment consisted of an open 250-cm^3 stirred reaction flask, partially submerged in a constant temperature bath. Total liquid volume in each experiment was 200 cm^3. Chloride concentration of the reaction liquid was monitored by a chloride-sensitive electrode (Fisher Scientific). The electrode was calibrated after each run by using standard sodium chloride solutions that were adjusted to temperature and acidity of the experiment. Dissolved chlorine was monitored at 322 nm by a Milton Roy Spectronic 1201 UV spectrophotometer equipped with a 0.4-cm^3 flow cell with a 1-cm path length. The extinction coefficient for chlorine was confirmed at a constant value ($\epsilon = 75$) over the range of acidities of this study by iodometric titration. Liquid was continuously pumped at 100 cm^3/min from the reaction flask through the flow cell and back to the flask. Residence time in this recycle system was about 6 s.

In each experiment, sulfuric acid solution was brought to constant reaction temperature (±0.5 K) in the reaction flask. Chlorine gas (99.9%) from a lecture bottle (Matheson Co.) was bubbled through the solution via a fritted glass sparger. The chlorine concentration was maintained constant by making fine adjustments to the flow so that the rate of input balanced the rate of evaporation of chlorine from the liquid surface in the open flask.

After chlorine concentration achieved a constant value, formic acid (Fisher Scientific, 88% HCOOH aq) was added to the flask. The concentrations of chloride and chlorine were then monitored as functions of time, usually for 15–90 min, depending upon the rate of reaction. Chlorine concentration was maintained constant as before.

Experiments were conducted over the following range of conditions: temperature, 288–328 K; sulfuric acid concentration, 1–4 M; formic acid concentration, 0.1–0.9 M. Experimental data were recorded only up to the time that the calculated formic acid conversion was 3% or less.

To compute the relationship between measured chloride concentration and carbon dioxide concentration, we assumed that the stoichiometry is determined by the reaction of chlorine and formic acid

$$Cl_2 + HCOOH \rightarrow 2H^+ + 2Cl^- + CO_2 \qquad (6)$$

and the equilibrium hydrolysis of chlorine

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (7)$$

The equilibrium formation of Cl_3^-

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^- \qquad (8)$$

was neglected because it has a reported equilibrium constant[6] of 0.191 at 25 °C. At the chlorine concentration of this study, less than 0.6% of chloride would be converted to Cl_3^-. Since the experiments were conducted at constant chlorine, formic acid, and sulfuric acid concentration, the relationship between carbon dioxide and chloride concentration is (see Appendix)

$$[CO_2] = \frac{1}{2}\left([Cl^-] - \frac{[Cl^-]_0^2}{[Cl^-]}\right) \qquad (9)$$

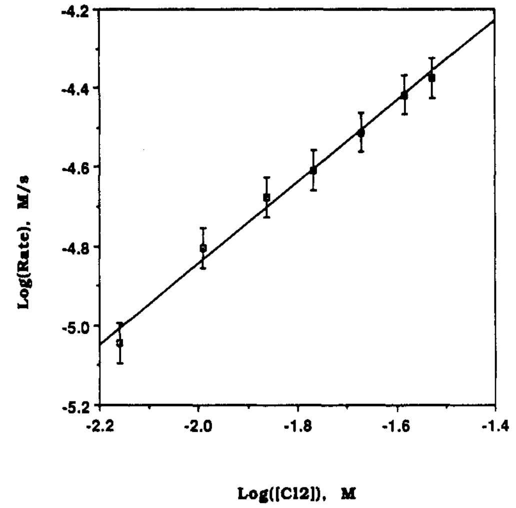

Figure 1. Rate dependence on chlorine at 298 K, 0.7 M HCOOH, and 1 M H_2SO_4.

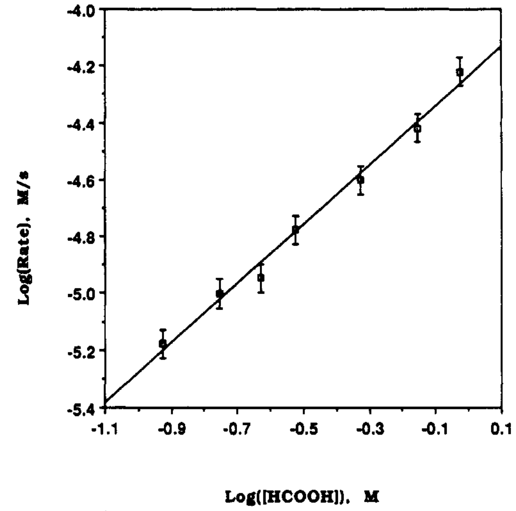

Figure 2. Rate dependence on formic acid at 298 K, 0.03 M Cl_2, and 1 M H_2SO_4.

Results

In determining reaction orders for the formation of carbon dioxide, one reactant concentration was varied while others held constant in a series of experiments. Orders were calculated from the slopes of the appropriate logarithmic rate–concentration plots. Figure 1 shows the rate versus chlorine concentration at 0.7 M HCOOH, 1 M H_2SO_4, and 298 K. The order in chlorine is 1.02 ± 0.05. Figure 2 shows the rate versus formic acid concentration at 0.03 M Cl_2, 1 M H_2SO_4, and 298 K. The order in HCOOH is 1.04 ± 0.05. Figure 3 shows log (rate) versus H_- at 0.03 M Cl_2, 0.3 M HCOOH, and 298 K. The order in h_- is −0.93 ± 0.02. The acidity scale, H_-, previously determined for the bromine–formic acid system at 298 K,[5] was used over the entire temperature range of the present study. There is some justification for this assumption in view of the behavior of the Hammett acidity, H_0, which is relatively constant with temperature for H_2SO_4 solutions in the concentration range used.[7]

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(5) Cox, B. G.; McTigue, P. T. *J. Chem. Soc.* **1964**, 3893.

(6) Zimmerman, G.; Strung, F. C. *J. Am. Chem. Soc.* **1957**, *79*, 2063.

(7) Tickle, P.; Briggs, A. G.; Wilson, J. M. *J. Chem. Soc. B* **1970**, 65.

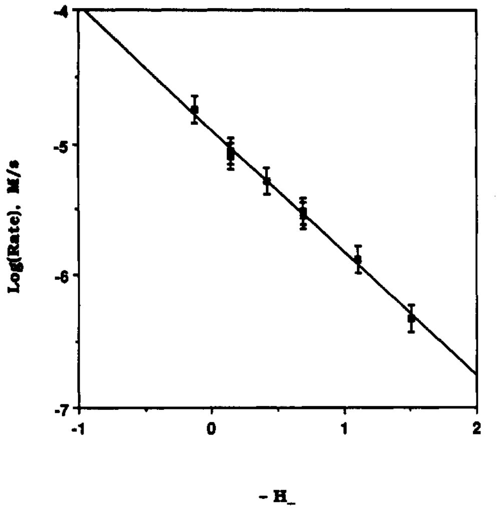


Figure 3. Rate dependence on acidity at 298 K, 0.3 M HCOOH, and 0.03 M Cl_2.

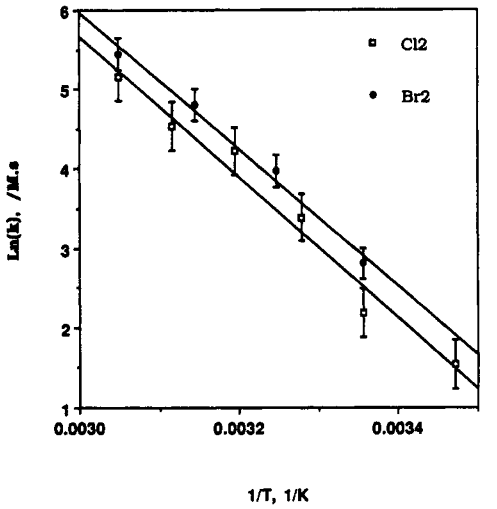


Figure 4. Temperature dependence on rate coefficients for chlorine–formic acid (squares) and bromine–formic acid (circles) reactions.

In summary, the chlorine–formic acid reaction follows first-order kinetics in chlorine and formic acid and approximately negative first-order behavior in acidity function, H_-. These orders are in agreement with previous studies of the bromine–formic acid system.[4,5] The kinetics of this reaction can be described by the rate law, in terms of carbon dioxide formation

$$d[CO_2]/dt = kK_a[HCOOH][Cl_2]/h_- \qquad (10)$$

At 298 K, the temperature at which most of the experiments were conducted, the experimental constant, kK_a in eq 10, is 0.0015 ± 0.0001 s^{-1}. With a reported pK_a value of 3.77,[8] the rate coefficient, k, for the formation of carbon dioxide is 8.8 ± 0.2 $M^{-1}\ s^{-1}$. By a similar procedure, a rate coefficient for the disappearance of bromine in the bromine–formic acid reaction is 16.4 $M^{-1}\ s^{-1}$. This latter value is about 20% lower than the value, 20.1 $M^{-1}\ s^{-1}$, reported by previous workers.[5] They did not report any loss of bromine from the liquid surface of the reactor. In the present study, the loss was substantial (equivalent on the order of 10–20% of the reaction rate) and had to be accounted for by a blank experiment that was run in the absence of formic acid.

Figure 4 shows Arrhenius plots for both the chlorine–formic acid and bromine–formic acid systems. The k's were determined from kK_a values, measured experimentally, and K_a values, estimated from heats of ionization that were reported in the literature. A heat of ionization, −0.54 kJ/mol, was reported[9] based upon microcalorimetric measurements at 298 K. In another study,[8] the effect of temperature on pK_a was determined for formic acid in aqueous solutions containing 3.1–100% ethylene glycol by an electrometric method. These data were extrapolated to 0% ethylene glycol and an average heat of ionization value of −0.84 kJ/mol determined for the temperature range 288–328 K. For purposes of the present study this value is in good agreement with the earlier study.[9] Both studies show that K_a is relatively constant over this temperature range.

TABLE I: Kinetic Parameters

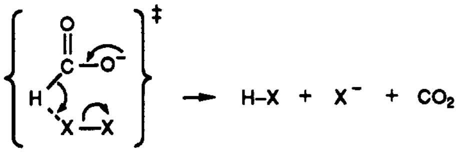
system	$A \times 10^{-14}$, $M^{-1}\ s^{-1}$	E, kJ/mol	$\Delta H^{\ddagger}$, kJ/mol	$\Delta S^{\ddagger}$, J/mol·K
$Cl_2/HCOOH$	1.0 ± 0.2	73.7 ± 6.0	70.7 ± 5.0	15.9 ± 1.7
$Br_2/HCOOH$	0.6 ± 0.1	71.6 ± 5.4	69.1 ± 5.4	10.0 ± 1.3

TABLE II: Properties of Chlorine and Bromine

species	electron affinity of atom, kJ/mol	dissociation enthalpy of molecule, kJ/mol	difference (net heat release), kJ/mol
Cl_2	349	242	107
Br_2	325	193	132

Table I shows the activation energies, E, and preexponential factors, A, determined from the slopes and intercepts of the fitted lines in Figure 4. The activation energy values for the two reaction systems are almost identical. Also shown are $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameters determined from ln (k/T) vs $1/T$ plots.

A comparison of the kinetic parameters for the two reaction systems (Table I) indicates that they are energetically similar. Small $\Delta S^{\ddagger}$ values (ca. 10–16 J/mol·K) are indicative of an activated complex of a formate ion and halogen molecule, X_2, associated together with elongated C–H and X–X bonds:



The formation of H–X should energetically favor the chlorine–formate reaction since the H–Cl bond energy is greater than that of H–Br. However, a consideration of the breaking of X–X bonds and electron affinity of X atoms (Table II)[10] favors the bromine–formic acid reaction, as observed.

Acknowledgment. We gratefully acknowledge financial support for this work from Eka Nobel Inc.

Appendix: Derivation of Eq 9

From the stoichiometry of the reaction system eq 6 and 7, chloride concentration can be described by the expression

$$[Cl^-] = 2[CO_2] + [HOCl] \qquad (A1)$$

Assuming the equilibrium is established quickly for chlorine hydrolysis

$$K_{eq} = [HOCl][H^+][Cl^-]/[Cl_2] \qquad (A2)$$

Combining these two expressions

$$[Cl^-] = 2[CO_2] + K_{eq}[Cl_2]/[H^+][Cl^-] \qquad (A3)$$

At the beginning of an experiment, pure chlorine is dissolved to form a solution establishing equilibrium concentrations of chloride and hypochlorous acid in equimolar amounts. Therefore K_{eq} can be expressed as

$$K_{eq} = [H^+][Cl^-]_0^2/[Cl_2] \qquad (A4)$$

Both proton and chlorine concentrations remain constant during an experiment. Combining eqs A3 and A4, we obtain

$$[Cl^-] = 2[CO_2] + [Cl^-]_0^2/[Cl^-] \qquad (A5)$$

which is rearranged to give eq 9.

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(9) Lebed, V. I.; Mamina, E. A.; Bondarev, N. V. *Russ. J. Phys. Chem.* **1986**, *60*, 1299.

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 543.