Gas Evolution Oscillators. 2. A Reexamination of Formic Acid Dehydration[1]

Kenneth W. Smith,[2,3a] Richard M. Noyes,* and Peter G. Bowers*[3b]

Department of Chemistry, University of Oregon, Eugene, Oregon 97403 (Received: December 14, 1982)

At formic acid concentrations of about 0.3 M in warm concentrated sulfuric acid, carbon monoxide is evolved smoothly whether the solution is stirred or not. If such a solution is rapidly stirred, decay of formic acid obeys clean irreversible first-order kinetics. If the solution is not stirred, the concentration of dissolved carbon monoxide rises to a limit of about 0.07 M; this value is about 80 times the equilibrium solubility at 1 atm. In an unstirred solution, the system approaches a "pseudoequilibrium" in which the concentrations of dissolved HCOOH and CO are about equal. If the concentration of formic acid is increased to about 4 M, gas is evolved from a gently stirred solution in oscillatory pulses. The amount of gas evolved during a pulse decreases with successive pulses, the maximum change in dissolved-gas concentration being approximately 0.07 M per pulse. These observations indicate that the oscillations result from repetitive release of supersaturation by homogeneous nucleation; they invalidate the purely chemical explanation developed by Showalter and Noyes. Supersaturations of up to 80-fold suggest that formic acid in concentrated sulfuric acid can generate carbon monoxide in situ at concentrations that could otherwise only be attained with high-pressure apparatus.

Introduction

Although a previous paper[1] has shown that oscillatory gas evolution from a chemical reaction is more common than was previously realized, the original Morgan reaction[4] remains one of the best examples of this kind of process. The reaction takes place in concentrated sulfuric acid at moderately elevated temperatures and the net chemical change can be described by the trivially simple stoichiometry of eq 1:

$$HCOOH(soln) \rightarrow CO(g) + H_2O(soln) \qquad (1)$$
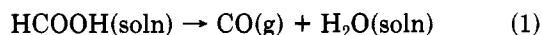
Compared to other gas evolution oscillators, oscillations in the Morgan reaction occur over a wider range of concentration and temperature, exhibit a broader range of frequency and amplitude, continue for a longer time period, and with care are relatively reproducible. In addition there is a wealth of information on the overall (nonoscillatory) kinetics and mechanism of the reaction.

The rate of gas evolution can be followed conveniently by monitoring the pressure in a reaction flask connected to the atmosphere by a capillary leak as described elsewhere.[2] Figure 1 illustrates the traces that were obtained for two such runs that were identical except that the rate of gently stirring in one was about twice that in the other. Because of the strong dependence of behavior on stirring, we can only define semiquantitatively the conditions under which oscillations are possible. We have observed oscillations between 20 and 65 °C but could not obtain them with formic acid concentrations less than about 1 M, or with sulfuric acid less than about 70%.

For temperatures or acidities too low for oscillations, the mixture emits a single burst of gas and then settles down to smooth evolution. The maximum observable frequency of oscillations is limited by the physical ejection of material from the reaction flask. For formic acid concentrations below about 0.05 M, even bubble formation is minor in unstirred solutions.

If a chemical process can truly be described by a simple stoichiometry like that of eq 1, the rate can be followed by monitoring either the product formed or the reactant consumed. If rates measured in these ways fail to coincide even for modest transient periods, significant material is then being held up in the form of intermediates. Showalter and Noyes[5] reasoned that dissolved carbon monoxide was the only conceivable major intermediate and that the presence of some bubbles at all times meant that bulk concentration of dissolved CO never deviated much from that for a solution saturated at 1 atm. They therefore concluded that a trace like that in Figure 1 also measured changes in the rate of consumption of formic acid. The fallacies in their argument will become apparent below.

The present paper will provide a brief history of previous work and will then report new observations, particularly centered on the effect of agitation on the rate of gas release. These experiments were performed in both oscillatory and nonoscillatory regions of the reaction and indicated startlingly high dissolved-gas concentrations. The interpretation of our observations explains many of the difficulties with previous reports and leads to what we now consider to be a satisfactory qualitative explanation of the oscillations.

Previous Kinetic Measurements of Reaction 1

The quantitative study of the kinetics of formic acid dehydration began almost a century ago. Because of available analytical techniques, all rate measurements during the first half century had to be based on product gas formation, and this approach was continued to the other studies prior to the present one. The published studies are by no means consistent with each other.

Veley[6-8] made the first kinetic measurements. He apparently did not stir the solutions but found that the rate of gas evolution was increased by adding material like silica or pumice. He recognized that supersaturation could be a problem with interpreting the data but claimed that the reaction was second order in dissolved formic acid.

Lamplough[9] stirred his solutions and obtained first-order kinetics. Meyer[10] shook the reaction flask and also obtained good first-order kinetics—but only after glass

(1) Paper No. 52 in the series "Chemical Oscillations and Instabilities". Paper No. 51 is Bowers, P. G.; Noyes, R. M. *J. Am. Chem. Soc.*, in press.
(2) Based in part on: Smith, Kenneth W. Ph.D. Thesis, University of Oregon, Eugene, OR, 1981.
(3) Present addresses: (a) Exxon Research and Engineering Co., P. O. Box 51, Linden, NJ 07036; (b) Department of Chemistry, Simmons College, 300 The Fenway, Boston, MA 02115.
(4) Morgan, J. S. *J. Chem. Soc., Trans.* **1916**, *109*, 274–83.

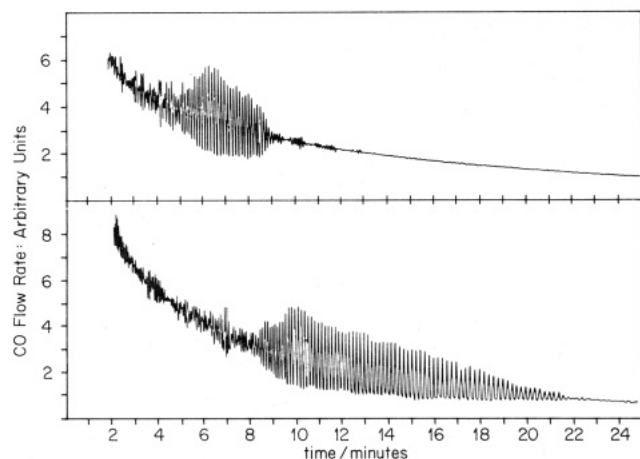(5) Showalter, K.; Noyes, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 1042–9.
(6) Veley, V. H. *Philos. Trans. R. Soc. London, Ser. A* **1888**, *179*, 257–95.
(7) Veley, V. H. *Philos. Mag.* **1903**, *6*, 271–9.
(8) Veley, V. H. *Trans. Faraday Soc.* **1909**, *5*, 1–14.
(9) Lamplough, F. E. E. *Proc. Cambridge Philos. Soc.* **1908**, *14*, 580–608.
(10) Meyer, J. *Z. Elektrochem.* **1909**, *15*, 506–9.

Figure 1. Rate of gas evolution at 55 °C in arbitrary units from two solutions each prepared by injecting 8.0 mL of 23.4 M formic acid into 20 mL of 96% sulfuric acid. Both solutions were stirred gently to moderately, but the upper solution was stirred about twice as rapidly as the lower one was.

spheres had been added to reduce supersaturation.

Morgan[4] was the first to report oscillatory gas evolution during this reaction. He clearly thought that supersaturation was involved and noted that Findlay and King[11] had reported oscillatory gas evolution when the pressure was suddenly released on an aqueous solution saturated with carbon dioxide at high pressures. The Findlay and King report may be the first known example of a gas evolution oscillator.

This oscillatory gas evolution was also studied by Okaya,[12] who was interested in other periodic phenomena including Liesegang rings[13] and heterogeneous catalysis of hydrogen peroxide decomposition.[14]

Schierz[15] summarized the previous literature and made careful kinetic studies at different temperatures and concentrations of acid. He recognized the potential complications of supersaturation and added short pieces of glass rod to the reaction flask, which was well shaken during a run.

Similar precautions against supersaturation were taken by Shierz and Ward,[16] and by DeRight.[17] Hammett[18] related the rates to the H_0 acidity function and reached apparently valid conclusions about the mechanism of the reaction. The claim of oscillations had by then vanished into oblivion, and there is no evidence that either DeRight[17] or Hammett[18] was aware of the claims of Morgan[4] and Okaya.[12]

Interest in this reaction revived when isotope effects became important to mechanistic chemistry. Ropp et al.[19] looked at the decomposition of ^{14}C-labeled formic acid. They only examined gas obtained after the first 30% of the reaction so that all the air initially present had been removed, and they stopped at 70% reaction because of kinetic anomalies at long times.

Ropp[20] subsequently reported further studies in which more severe kinetic anomalies were noted. Each run ex-

hibited an induction period before the maximum rate of gas evolution was attained. That induction period was alleged to be too long to be explained either by the mixing of the formic and sulfuric acids or by the saturation of the solution, but no quantitative data were provided. Ropp also reported deviations from first-order decay at long times and an acceleration of gas evolution if powdered glass was added.

By the time of the Ropp[19,20] studies, technology had made possible a magnetic stirring much more convenient than the cumbersome shaking of two or three decades previous, but these magnetically stirred solutions exhibited kinetic anomalies much more serious than any referred to in the studies of formic acid decomposition in the 1920s and 1930s. The discussion to follow will make it seem probable that the Ropp experiments were significantly affected by supersaturation. "Progress" in chemical technique is not always unidirectional!

Ropp[20] also reported isotopic exchange of [18]O between carbon monoxide and sulfuric acid. That observation may be significant to the conclusions to be described below.

The final chapter in this history began when Showalter and Noyes (SN)[5] discovered an arcane reference to the Morgan reaction in a review of oscillatory phenomena by Nicolis and Portnow.[21] SN found it almost ridiculously easy to obtain oscillations and became fascinated with the phenomenon. They approached it from a background of purely chemical oscillators and used wishful thinking and the kinetic anomalies of Ropp to conclude that the system was more complicated chemically than was suggested by the straightforward studies of the 1920s and 1930s. This interpretation was assisted by the remarkable effect of formaldehyde on the oscillating system; a dramatic illustration can be found in Figure 2 of ref 5. The misconceptions led to a fanciful chemical monstrosity which was chiefly constructed by the senior author of that paper, who herewith retracts it.

Bowers and Rawji[22] became interested in the oscillations at about the same time. They were impressed with the heavy foaming and obtained analytical data that indicated the foam was depleted in formic acid relative to the bulk liquid. Their explanation of the oscillations included a different rate of formic acid decomposition in the surface of the foam and in the bulk solution. In view of the fact that gas evolution oscillators are now known in which no foam is produced,[1] the explanation of Bowers and Rawji is also no longer tenable.

Experimental Details

Reagents. Baker Analyzed Reagent grade formic and sulfuric acids were used as received. A few experiments with distilled formic acid and with boiled and degassed sulfuric acid produced kinetic behavior comparable to that with untreated reagents.

Sulfuric acid stock solution was analyzed by titrating weighed samples with standard base. Less concentrated acids were prepared gravimetrically by careful dilution with water.

Analysis for Formic Acid. Formic acid concentrations during a run were determined spectrophotometrically. Because of gas bubbles in the reacting medium, it usually was not possible either to measure absorbance directly or to withdraw an aliquot volume. The procedure was to withdraw about 0.5 mL of solution with a disposable pipet, mix it in about 10 mL of water that had previously been weighed to the nearest milligram, reweigh, and make up

(11) Findlay, A.; King, G. *J. Chem. Soc., Trans.* **1913**, *103*, 1170–93.
(12) Okaya, T. *Proc. Phys.-Math. Soc. Jpn.* **1919**, *1*, 43–51.
(13) Okaya, T. *Proc. Tokyo Math.-Phys. Soc.* **1918**, *9*, 442–62.
(14) Okaya, T. *Proc. Phys.-Math. Soc. Jpn.* **1919**, *1*, 283–94.
(15) Schierz, E. R. *J. Am. Chem. Soc.* **1923**, *45*, 447–55.
(16) Schierz, E. R.; Ward, T. *J. Am. Chem. Soc.* **1928**, *50*, 3240–3.
(17) DeRight, R. E. *J. Am. Chem. Soc.* **1933**, *55*, 4761–4.
(18) Hammett, L. P. "Physical Organic Chemistry"; McGraw-Hill: New York, 1940; pp 277–8, 283–4.
(19) Ropp, G. A.; Weinberger, A. J.; Neville, O. K. *J. Am. Chem. Soc.* **1951**, *73*, 5573–5.
(20) Ropp, G. A. *J. Am. Chem. Soc.* **1960**, *82*, 842–52.

(21) Nicolis, G.; Portnow, J. *Chem. Rev.* **1973**, *73*, 365–84.
(22) Bowers, P. G.; Rawji, G. *J. Phys. Chem.* **1977**, *81*, 1549–51.

to 25 mL volumetrically. Absorbance was then measured at 205 nm where Beer's law was obeyed with an extinction coefficient of 44.7 M^{-1} cm^{-1}. Carbon monoxide does not absorb at this wavelength. Reactions involving very low (less than 0.05 M) formic acid concentrations could be run in an in-place spectrophotometer cell for several hours before any gas bubbles formed.

Measurement of Pressure. Pressures were measured with Celesco KP-15 and P7D variable reluctance differential pressure transducers driven by a CD-25 transducer indicator. The output of the CD-25 was connected to a chart recorder. The transducers were calibrated with a U-tube water manometer.

Total evolved gas could be calculated from the difference in pressure between the reaction flask and a closed reference flask in the same thermostat bath. Such pressure differences could usually be measured to within 1%.

Rate of gas evolution could be determined by fitting the reaction flask with a capillary leak and measuring the pressure difference between the flask and the surroundings. The capillary was about 10 cm long and 0.5 mm in diameter. Although laminar flow in such a capillary is a nonlinear function of difference in pressure, the absolute pressure in the flask never differed by more than about 1% from that outside, and decay of excess pressure could be regarded as a simple exponential. The flow through the capillary was 0.02 mol atm^{-1} s^{-1}, and with 50 mL in the reaction flask the rate constant for pressure decay was about 10 s^{-1}. Such an arrangement could resolve individual oscillatory pulses up to about 10 per minute. Figure 1 is an example of the wave-form curve obtained with this arrangement. For quantitative measurements of time period and amplitude of the oscillations the capillary leak was omitted so that the transducer output resembled a step-form trace such as that in Figure 3b of the previous paper.[1]

Mixing of the Reactants. Experiments in the nonoscillatory region of reaction involved dilute solutions (less than about 0.5 M) and were prepared by introducing formic acid from a hypodermic syringe through a serum cap on one neck of a three-necked flask containing thermostated sulfuric acid. For more concentrated solutions, such as those giving rise to oscillations, the formic acid was cooled in ice before being quickly poured into the sulfuric acid. Precooling prevented excessive temperature rises due to heat of mixing. In all cases the viscous solutions needed to be well shaken for several seconds to ensure complete mixing.

Agitation. The reaction vessel could be stirred magnetically. "Gentle" or "moderate" stirring kept the flask contents well mixed and thermally equilibrated but did not pull gas into the liquid. "Rapid" stirring pulled the central vortex down deeply enough that bubbles were constantly sucked into and dispersed through the solution. The evidence presented below leads us to believe that rapid stirring (or vigorous manual shaking) virtually eliminated supersaturation in the solution. Solutions that would have exhibited oscillations with gentle or even moderate stirring decayed with smooth first-order kinetics when subjected to rapid stirring.

Experiments with Formaldehyde. These were made with either formalin solution, mixed with sulfuric acid just before initiating a reaction, or with sublimed trioxane, mixed with sulfuric acid several hours before use to ensure complete depolymerization. Reaction products in these experiments were extracted with diethyl ether after neutralizing the strong acid solvent. They were identified by IR and mixed melting point.
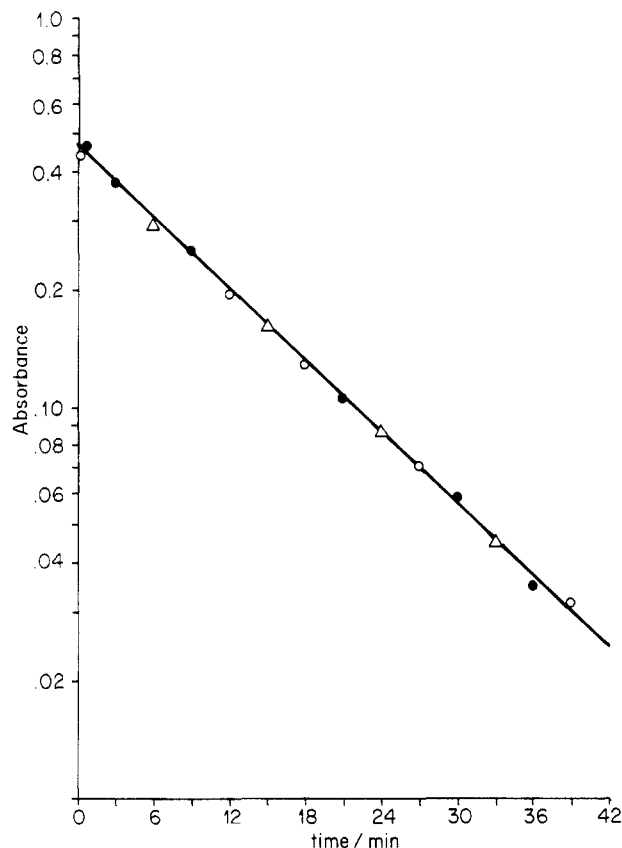
Figure 2. Change of formic acid absorbance with time for three runs at 40.1 °C each prepared by adding 1 mL of 23.4 M formic acid to 100 mL of 90% sulfuric acid. Each run was stirred by bubbling gas through it. Gases: (O) N_2; (●) CO; (△) O_2.

Equilibrium Solubility Studies. The solubility of carbon monoxide in sulfuric acid was measured by a modification of the Bunsen method.[23] A measured volume of sulfuric acid was degassed and carbon monoxide was admitted to the known volume of evacuated space above the unstirred acid. The pressure was measured immediately after the gas was introduced and again after equilibrium with the liquid had been attained.

Results of Nonoscillatory Chemical Studies

Effects of Different Gases on Rates of Reaction. A key assumption in the SN mechanism is a major effect of product carbon monoxide on the rate of consumption of formic acid. The spectrophotometric procedures described above permit a test of that assumption. Figure 2 is a composite of data from three runs in which the reaction mixture was stirred by introducing a rapid stream of gas. Decay of formic acid is followed well over 90% of the way to completion as an excellent first-order process, with no influence on the rate from the composition of the gas stream.

Kinetic Anomality I. The Induction Period. Ropp[20] measured rate of product gas formation and reported kinetic problems resulting from an induction period before gas evolution reached a maximum. The curve in Figure 3 illustrates how the induction period arises in an insufficiently stirred solution as it becomes supersaturated. Although such a solution lags behind in the amount of *evolved* gas, as soon as the solution is agitated all the dissolved gas is rapidly given up. Evidently the reaction producing carbon monoxide is proceeding smoothly whether or not gas is being evolved. In support of this

(23) Bunsen, R. "Gasometrische Methoden", 2nd ed.; Vieweg: Braunschweig, 1877.
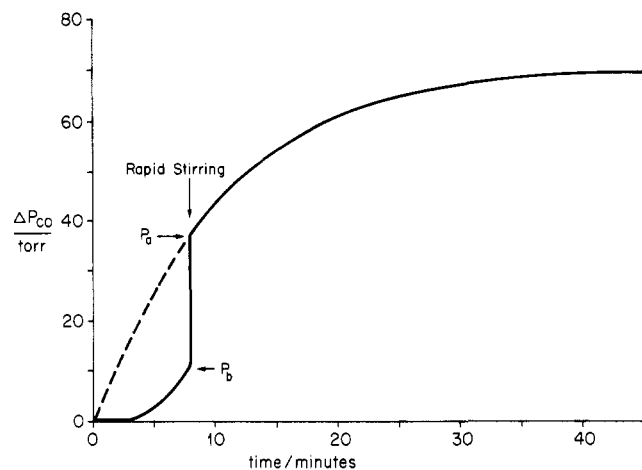
Figure 3. Gas evolution from a run at 40.1 °C containing 0.230 M formic acid in 95% sulfuric acid. The system was not stirred at first, but rapid stirring was initiated at the point marked P_b and then continued. The dashed curve is the behavior of an identical system that was subject to rapid stirring throughout.
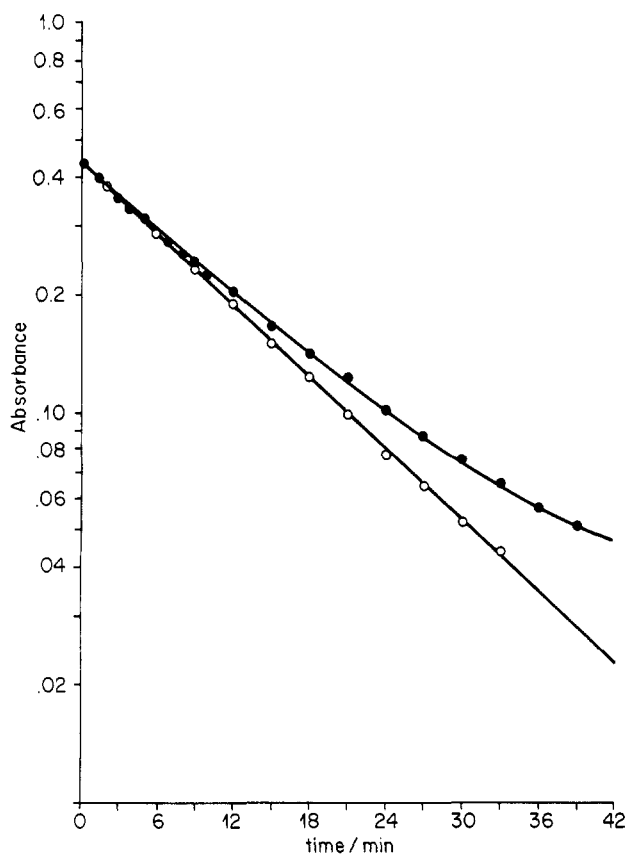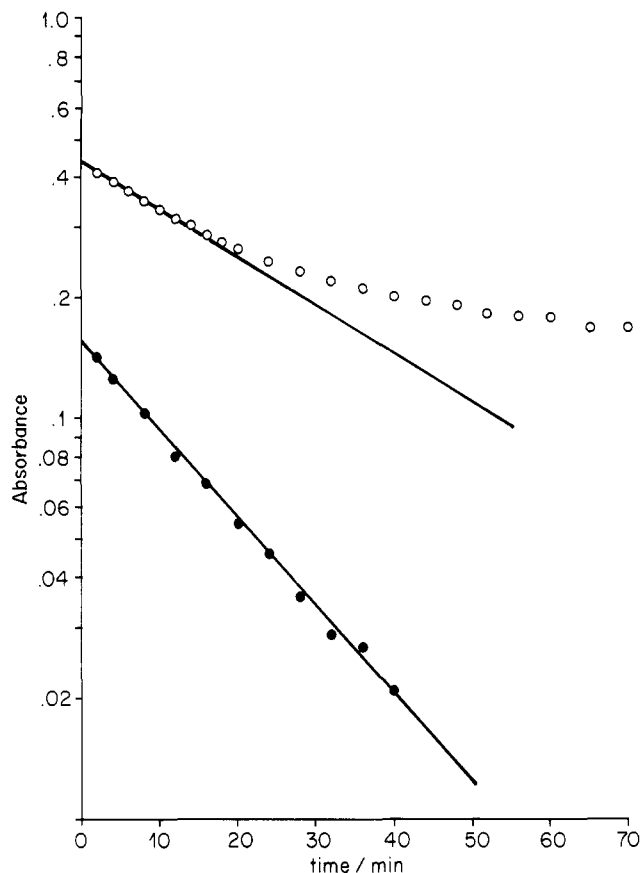

Figure 4. Change of formic acid absorbance with time for two runs at 40.1 °C each prepared by adding 1 mL of 23.4 M formic acid to 100 mL of 90% sulfuric acid: (●) solution unstirred; (O) solution subject to rapid stirring.

explanation of the induction period, Figures 2 and 4 show clearly that there is *no* induction period for the disappearance of formic acid in solutions agitated either by a gas stream or by rapid stirring.

We conclude that in Ropp's work the solutions were not stirred sufficiently rapidly to eliminate supersaturation.

Kinetic Anomaly II. The Reversibility of Formic Acid Consumption. Figure 2 and the lower curve in Figure 4 demonstrate that in a rapidly stirred solution formic acid decays by relatively clean irreversible first-order kinetics. However, the upper curve in Figure 4 indicates that formic acid at an initial concentration of about 0.23 M decomposes more slowly if the solution is unstirred than if it is stirred.


Figure 5. Change of absorbance with time at 40.1 °C of a 0.046 M solution of formic acid in 92% sulfuric acid. Absorbance could be measured directly because no visible gas bubbles formed in this very dilute solution during the time of the run. (O) log A_t. (●) log $(A_t - A_{t+\Delta})$ where Δ = 16 min.

Figure 5 shows a still more dilute solution which was prepared by adding 0.010 mL of 23.4 M formic acid to 5.1 mL of 92% sulfuric acid in a cylindrical spectrophotometer cell with light path 2.00 cm. The solution was dilute enough that bubbles did not form and direct spectrophotometric measurements were therefore possible.

The absorbance in Figure 5 decayed initially as expected with a rate constant of 4.7×10^{-4} s^{-1} in good agreement with the 4.5×10^{-4} s^{-1} observed for rapidly stirred solutions of 92% sulfuric acid containing somewhat larger concentrations of formic acid. At longer times the absorbance approaches a limiting value of about 0.17. Figure 5 also shows a Guggenheim[24] plot of log $(A_t - A_{t+\Delta})$ where Δ = 16 min. This treatment generates a good straight line with slope corresponding to a decay constant of 8.7×10^{-4} s^{-1}.

Because CO is escaping only very slowly from the solution in Figure 5, the system approaches a "pseudoequilibrium" as in eq 1a. The concentration of

$$\text{HCOOH(soln)} \rightleftarrows \text{CO(soln)} + \text{H}_2\text{O(soln)} \qquad (1a)$$
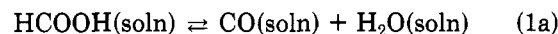
water in 92% sulfuric acid is much more than the 0.046 M initial concentration of formic acid, and we can describe approach to the pseudoequilibrium by first-order rate constants k_f and k_r to generate eq 2. The Guggenheim

$$[\text{CO}]/[\text{HCOOH}] = k_f/k_r = K \qquad (2)$$

plot in Figure 5 gives $k_f + k_r$, and we obtain $K = 4.7 \times 10^{-4}/(4.0 \times 10^{-4}) \simeq 1.2$. The pseudoequilibrium concentration of CO in this experiment is 0.025 M, which is much more than the 1.0×10^{-3} M equilibrium concentration in

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(24) Guggenheim, E. A. *Philos. Mag.* **1926**, *2*, 538–43.

TABLE I: Solubilities of CO at 25 °C in Various Solvent Compositions

H_2SO_4, %	10^4(solubility at 1 atm), M	concn of gas released by rapid stirring of reaction mixture, M
90.0	8.4 ± 0.3	0.050 ± 0.004
91.0	8.6 ± 0.6	0.054 ± 0.005
92.0	8.9 ± 0.6	0.056 ± 0.008
93.0	9.3 ± 0.6	0.064 ± 0.008
94.0	9.3 ± 0.6	0.068 ± 0.009
95.0	9.9 ± 0.6	0.073 ± 0.010
96.0	10 ± 1	0.081 ± 0.010
97.0	10.7 ± 0.2	

contact with gas at 1 atm (see the measurements below).

The same sort of deviation from first-order behavior was also observed at 45 °C for total gas evolved from a much more concentrated (4.14 M) solution of formic acid that was oscillatory while subject to gentle stirring. If the stirring was rapid, the smooth gas evolution exhibited good first-order behavior.

The pseudoequilibrium interpretation of the nonlinearity in Figure 5 is also consistent with the claim of Ropp[20] that CO exchanges oxygen with isotopically labeled H_2SO_4.

Carbonylation of Formaldehyde. SN[5] noted the dramatic ability of formaldehyde, CH_2O, to inhibit oscillations and regarded the effect as strong evidence for the chemical nature of the oscillations. They thought the formaldehyde was scavenging radicals that would otherwise have caused formic acid to decompose with the production of CO.

In our experiments, a known amount of formaldehyde was added to a gently stirred Morgan reaction in progress. After gas evolution had resumed, the mixture was rapidly stirred until the end of the reaction to ensure complete evolution of CO. The amount of CO destroyed by CH_2O was calculated, the initial formic acid concentration being known. In a series of such runs, the ratio CO(destroyed)/CH_2O(added) was 1.05 ± 0.09 for formaldehyde from formalin, and 0.97 ± 0.02 for formaldehyde from trioxane. The organic product in the presence of formaldehyde was identified as glycolic acid, $CH_2OHCOOH$. These results lead us to suggest a 1:1 reaction between CO and CH_2O. Koch[25] has shown that carbonium ions can react by carbonylation and hydration to generate carboxylic acids. Protonated formaldehyde could form glycolic acid by the sequence of eq 3 and 4:

$$H_2COH^+ + CO \rightleftharpoons HOCH_2CO^+ \qquad (3)$$

$$HOCH_2CO^+ + H_2O \rightleftharpoons HOCH_2CO_2H + H^+ \qquad (4)$$

A referee subsequently pointed out to us that this very reaction was once used for the commercial production of glycolic acid! The ability of formaldehyde to inhibit gas evolution is therefore irrelevant to the SN mechanism.

Results of Studies of Supersaturation during Reaction

Equilibrium Solubility of Carbon Monoxide. The middle column of Table I shows the Henry's law constants for carbon monoxide in sulfuric acid at various concentrations. Our data are consistent with the early measurements of Christoff,[26] who reported a solubility of 8.9 × 10^{-4} M for CO in 96% sulfuric acid.

Of course, these solubilities include dissolved carbon monoxide in all forms and are really [CO] + [HCOOH].

(25) Koch, H. *Brennst.-Chem.* **1955**, *36*, 321.
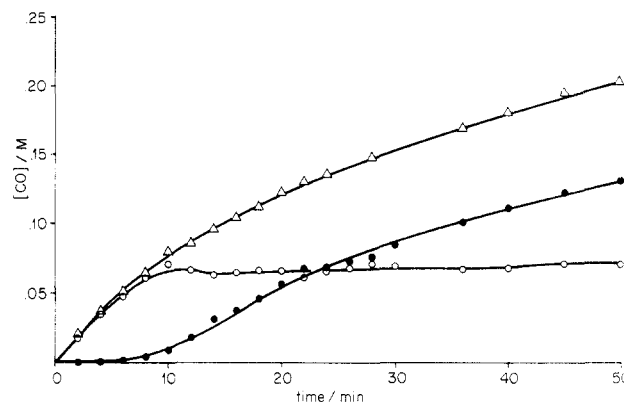(26) Christoff, A. *Z. Phys. Chem.* **1906**, *60*, 622–31.

Figure 6. Gas evolution at 25 °C from solutions containing 0.230 M formic acid in 92% sulfuric acid. At any time, $[CO]_E$ (●) is the gas evolved to that time from the previously unstirred solution, $[CO]_T$ (△) is the total gas evolution after rapid stirring had been initiated at that time, and $[CO]_{soln}$ (○) is the difference representing dissolved gas released by initiation of rapid stirring.

The equilibrium value of [CO] alone is even smaller than the entry in Table I and contrasts with the above analysis of Figure 5, which indicates that a solution containing 0.025 M CO produced chemically need not exhibit bubble formation. Major supersaturation is clearly possible, and we used two different methods to determine the level of supersaturation attained in a reacting solution.

Supersaturation in an Unstirred Solution. Measurements of pressure of evolved gas before and after vigorous stirring, which resulted in curves such as that in Figure 3, allowed determination of the concentration of dissolved carbon monoxide at various stages of the reaction. In these experiments, the initial concentration of formic acid was sufficiently low that oscillations did not occur. In a typical run, stirring was started at a predetermined time (gas pressure P_b in Figure 3) and resulted in a rapid release of carbon monoxide to give pressure P_a. Rapid stirring was continued to the end of the reaction at pressure P_∞. Then, at the time stirring was started, we can write eq 5.

$$[CO]_{soln} = \frac{P_a - P_b}{P_\infty}[HCOOH]_0 \qquad (5)$$

The results of such runs are shown in Figure 6. At each time, the three concentration points represent the results of a single run. $[CO]_T$ is the total amount of carbon monoxide produced by that time, $[CO]_E$ is the amount evolved before stirring started, and $[CO]_{soln} = [CO]_T - [CO]_E$ is the amount dissolved at that time. As can be seen, in the absence of stirring the concentration of dissolved gas builds up to a constant value which we consider a limiting supersaturation concentration $[CO]_{ss}$. That limiting value is 0.067 M in the example shown in Figure 6. Once $[CO]_{ss}$ has been attained, it remains constant for the rest of the reaction while gas is evolved smoothly from the unstirred solution.

What is remarkable is that the limiting supersaturation concentration is as much as 80 times the equilibrium solubility at 1 atm. The comparison is shown in the middle and right-hand columns of Table I.

The right-hand column of Table I also illustrates the sharp dependence of $[CO]_{ss}$ on sulfuric acid concentration. The value falls approximately linearly by almost a factor of 2 in going from 97% to 90% acid. We also found that $[CO]_{ss}$ did not depend much on formic acid concentration, at least for sufficiently dilute solutions. More detailed data are available elsewhere.[2]

Table II shows that the limiting supersaturation concentration changes surprisingly little with temperature in

TABLE II: Temperature Dependence in 92.0% H_2SO_4 of Limiting CO Concentration and of Rate of HCOOH Consumption

temp, °C	limiting $[CO]_{ss}$, M	rate constant, s^{-1}	temp, °C	limiting $[CO]_{ss}$, M	rate constant, s^{-1}
25	0.067	0.000 49	45	0.065	0.0044
35	0.065	0.001 6	55	0.056	0.012
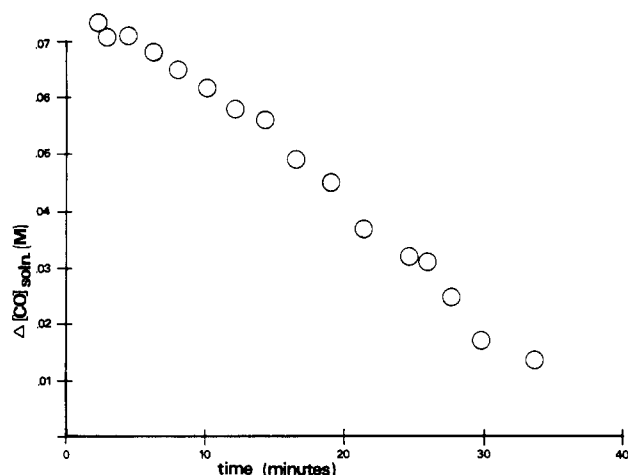
Figure 7. Concentrations of dissolved gas released during each pulse ($\Delta[CO]_{soln}$) of an oscillatory reaction at 45 °C. Initial concentrations were $[HCOOH]_0 = 4.14$ M, $[H_2O]_0 = 9.68$ M.

spite of the wide range in rates of formic acid dehydration.

Relief of Supersaturation during Oscillations. When gas evolution is followed by continuous monitoring of gas pressure above the solution, the result is a step-form curve. Under optimum conditions for oscillations in the Morgan reaction, no measurable gas evolution occurs between the pulses, and the curve has flat steps such as those shown in Figure 3b of the previous paper.[1] The vertical distance between successive steps (related to the amplitude of oscillatory gas evolution) measures the change in dissolved-gas concentration, $\Delta[CO]_{soln}$, per oscillation. After several small, irregular, and not readily measurable oscillations, $\Delta[CO]_{soln}$ decreases approximately linearly with time as shown in Figure 7. The maximum value that we observed was 0.073 M. This is in good accord with the value of $[CO]_{ss}$ shown in Table I and suggests that complete venting is occurring during the early oscillations. Then $\Delta[CO]_{soln} \simeq [CO]_{ss}$.

The decrease of $\Delta[CO]_{soln}$ with time during a run was presumably due in part to the effect of the water released during reaction 1. However, the decrease of $\Delta[CO]_{soln}$ in Figure 7 is more than would be anticipated from the variation of $[CO]_{ss}$ in the last column of Table I. Perhaps the bursts at long times are no longer venting all of the dissolved gas. A possible reason might be the formation of a smaller number of nuclei in each burst, but it seems premature to speculate on the basis of information presently available.

Discussion

Conclusions about Supersaturation. The observations reported above lead us unequivocally to the conclusion that in weakly stirred or unstirred solutions the concentration of dissolved CO can build up to about 0.07 M but will not go significantly above that value. Presumably this concentration represents the point at which rapid homogeneous nucleation of bubbles occurs. This concentration is 60–80 times that in a solution saturated at 1 atm. We were astounded when we first encountered ratios of this
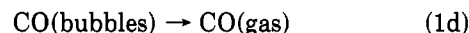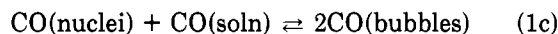
magnitude but see no other way to explain our observations.

Qualitative Explanation of the Oscillations. The evidence presented above indicates that oscillatory gas evolution occurs because the concentration of dissolved gas becomes so great that homogeneous nucleation initiates a rapid release. Showalter and Noyes[5] rejected such a possibility because bubbles were present in the solution at all times.

That argument failed to recognize that in time t a molecule diffuses a distance of the order of $(6Dt)^{1/2}$ where D is a diffusion coefficient of the order of 10^{-5} cm^2 s^{-1}. In 1 min a bubble can influence solution no more than about 1 mm away from it.

In an unstirred 0.3 M formic acid solution such as discussed above, a visible bubble will form on a wall or motionless stirrer, grow slowly for 1 min or more, and detach and rise slowly through the solution—yet the *average* concentration of dissolved gas in that solution corresponds to saturation at a pressure of several tens of atmospheres!

The mechanism as developed here might replace eq 1 by eq 1a–1d:

$$HCOOH(soln) \rightleftharpoons CO(soln) + H_2O(soln) \quad (1a)$$

$$CO(soln) \rightleftharpoons CO(nuclei) \quad (1b)$$

$$CO(nuclei) + CO(soln) \rightleftharpoons 2CO(bubbles) \quad (1c)$$

$$CO(bubbles) \rightarrow CO(gas) \quad (1d)$$

The distinction between bubbles and nuclei is arbitrary but is made because bubbles cannot dissolve completely without shrinking to nuclei and because nuclei are very unlikely to escape the solution without first growing to bubbles. Step 1d is written as irreversible because surface energy effects dictate that *any* population of bubbles or nuclei is unstable relative to a single continuous segment of gas phase.

The mechanism of eq 1a–1d is so simplistic that it does not lend itself satisfactorily to modeling. A more complete treatment, which recognizes the distribution of bubble sizes, and which satisfactorily accounts for at least most of the features of these oscillations, is presented in the paper immediately following.

Implication for Carbonylation Syntheses. Many synthetic reactions of both organic and inorganic chemistry employ carbon monoxide as a reagent. Yields can often be improved by running the reaction under pressure in an autoclave. If >90% sulfuric acid is a satisfactory reaction medium, and if the reaction of interest is rapid enough to consume CO as rapidly as it is generated from formic acid, a reaction that would otherwise require up to 80-atm pressure can be run conveniently without special equipment if formic acid is used as the reagent. Koch and Haaf[27] have already shown precisely this utility for the carbonylation of olefins, alcohols, alkyl chlorides, and esters.

Registry No. Formic acid, 64-18-6; carbon monoxide, 630-08-0.

(27) Koch, H.; Haaf, W. *Ann. Chem.* **1958**, *618*, 251–66.