has been changed but also its symmetry. We expect in these examples interesting consequences for the reactivity.

From the many examples which are possible we only chose a few representative ones to demonstrate our arguments. Including hetero systems there seems to be a large, interesting variety of molecules for which to study through-bond interactions. Synthetic efforts seem worthwhile to investigate the theoretical predictions.

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Oscillations in Chemical Systems. 24.[1] Oscillatory Decomposition of Formic Acid in Sulfuric Acid
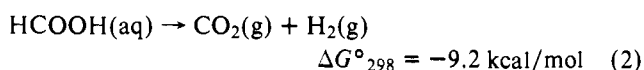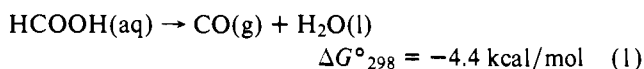
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Abstract: We have confirmed an observation reported by Morgan over 60 years ago that carbon monoxide is evolved in repetitive bursts when formic acid is heated to 55 °C in concentrated sulfuric acid. The principal dehydration-decarbonylation reaction cannot be based on acid catalysis as has been generally believed. Small additions of formaldehyde temporarily inhibit the reaction, and we have developed a mechanism based on hydroxyl radical catalysis of formic acid decomposition. That mechanism also invokes the very large increase in reduction potential of iron(III) salts due to carbonylation of impurities at the parts per million level. This reaction seems more useful than any other presently known to determine how far a system must be displaced from equilibrium before oscillations become possible.

Introduction

Aqueous formic acid is unstable with respect to decomposition to two different sets of products.

$$HCOOH(aq) \rightarrow CO(g) + H_2O(l)$$
$$\Delta G°_{298} = -4.4 \text{ kcal/mol} \quad (1)$$

$$HCOOH(aq) \rightarrow CO_2(g) + H_2(g)$$
$$\Delta G°_{298} = -9.2 \text{ kcal/mol} \quad (2)$$

Either process could be driven to completion, particularly if the product gases were vented. The various product species equilibrate at a negligible rate at ambient temperatures, and the products actually obtained from any system will be determined strictly by kinetic rather than by thermodynamic considerations.

Although dilute aqueous formic acid decomposes negligibly slowly, it is destroyed at a conveniently measurable rate in concentrated sulfuric acid, which is a strongly acidic dehydrating medium. The products coincide quantitatively with those of reaction 1. The reaction was studied over 60 years ago by Morgan,[2] who observed rapid pulses of gas evolution. He claimed that the periodic behavior depended upon the fraction used from his distillation of formic acid and noted an almost explosive reaction of formic acid if nitric acid was added. Morgan[2] concluded that the periodic behavior was probably
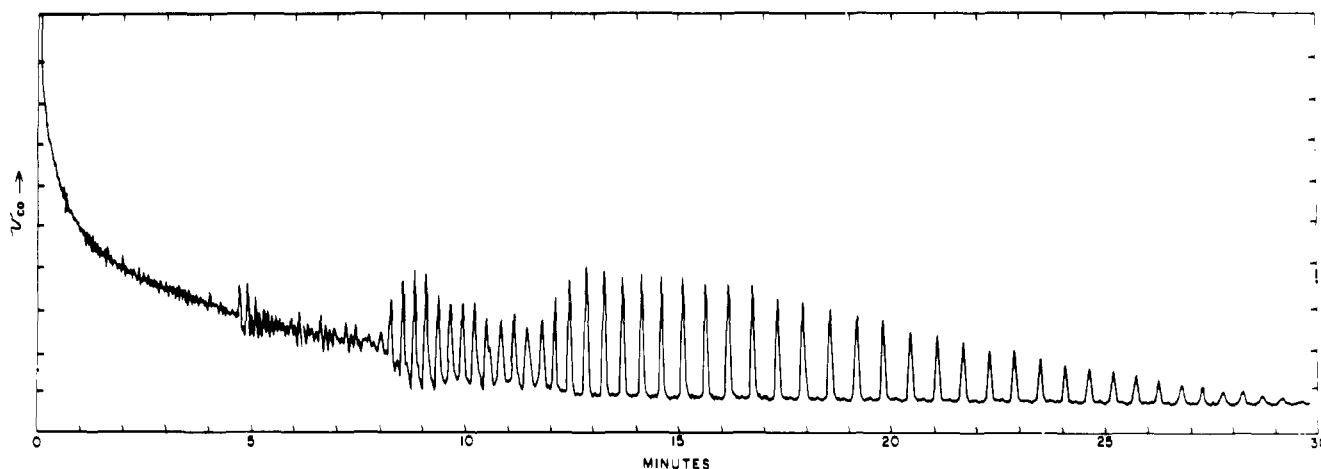
Figure 1. Rate of carbon monoxide production (in arbitrary units) at 55 °C by a stirred solution prepared from 8.0 mL of 88% aqueous formic acid and 20.0 mL of concentrated (ca. 97%) sulfuric acid. Stirring rate adjustments were made at 4.5 and at 8.0 min.

associated with release of supersaturation, although he made the significant observation that bubbles were always present in the solution even during periods of slow gas evolution.

Schierz[3] also ascribed the Morgan[2] observations to supersaturation and reported smooth gas evolution from agitated solutions. Hammett[4] subsequently showed that the logarithms of rates in different solvent compositions correlated excellently with his H_0 function. For several decades, the reaction has been regarded as an example of acid catalysis, and the Morgan[2] observations have been relegated to a footnote in reviews of oscillatory chemical reactions.

We have now reexamined the system and have duplicated most of Morgan's results. A similar study has been carried out simultaneously and independently by Bowers and Rawji[5] at Simmons College. They conclude that the oscillations are physical and are associated with supersaturation effects on an acid-catalyzed reaction. We note effects of additives that cannot easily be reconciled with simple acid catalysis, and we have developed an alternative chemical explanation that appears consistent with the known facts.

Experimental Section

Materials. The major reactants were J. T. Baker Co. Analyzed reagent grade concentrated sulfuric acid (about 97%) and formic acid (88%). They were usually used without further purification, although some samples of formic acid were fractionally distilled. A few experiments were also performed with J. T. Baker Co. Ultrex sulfuric acid, considered the purest (except for water) acid commercially available.

Other reagent grade commercial chemicals were concentrated nitric acid, $Fe_2(SO_4)_3 \cdot xH_2O$, KNO_3, absolute methanol, absolute ethanol, acetone, 37% formaldehyde, acrylamide, and 30% hydrogen peroxide. All were used without further purification.

Procedure. Unless otherwise noted, all reactant solutions were prepared by adding 4.0 mL of 88% formic acid to 10.0 mL of concentrated sulfuric acid. The reaction vessel consisted of a 30 × 200 mm test tube immersed in a water bath thermostated at 55.0 ± 0.2 °C. The solution was stirred with a variable speed magnetic stirrer. Evolved gas escaped through a capillary at the end of which it mixed with a carrier gas (helium or nitrogen) and immediately entered an Aerograph gas thermal conductivity cell. The signal was displayed with a Leeds and Northrop Speedomax recorder. In a few experiments the periodic evolution of CO was monitored spectrophotometrically at 2130 cm^{-1} with a Beckman Acculab 2 IR spectrophotometer and a flow-through cell with nitrogen carrier gas.

Analysis of Products. Analytical methods included infrared spectrophotometry, mass spectrometry, and chemical reaction. Although spectrophotometry could monitor CO production and could detect formic acid vapor, it was not sensitive enough to detect either carbon or sulfur dioxides.

Samples for mass spectrometry were bubbled through concentrated sulfuric acid to remove entrained formic acid and were analyzed with a CEC 21-110B high-resolution mass spectrometer. Samples so obtained were contaminated with some air. In order to correct for the contamination, samples of air and of product gas were analyzed at the same instrument settings. The CO_2/Ar ratio for the product gas was greater than for air while the O_2/Ar ratio was if anything less for the gas. The O_2 peak was used to determine how much of the mass 28 peak could be ascribed to N_2 from air, and the difference was assigned to CO by means of the assumption that CO and N_2 had equal ionization efficiencies. The procedure was crude but was sufficient to establish that CO_2 from the reaction was never as much as 0.1% of CO.

Chemical analyses were carried out in a nitrogen-purged glove bag with solutions made from boiled water and stored under nitrogen. Product gas from a Morgan reaction was bubbled through sodium hydroxide solution. Analysis for CO_2 was based on titration with standardized hydrochloric acid. Analysis for SO_2 was based on mild acidification, addition of a known amount of iodine solution, and titration with standardized thiosulfate. These chemical methods could only set upper limits on amounts of carbon and sulfur dioxides produced.

Results

Existence of Oscillations. The most important qualitative result of our experiments is a complete confirmation of the Morgan[2] claim of oscillatory gas evolution. A typical reaction sequence in a stirred solution is shown in Figure 1. Initial rapid evolution of gas takes place smoothly. Regular oscillations then develop and persist for up to 0.5 h. When a solution is oscillating regularly, bursts of gas evolution take place a few times per minute. During a burst, the solution becomes milky with many small bubbles and foams up rapidly. After this burst of foam, which is recorded as evolved gas in Figure 1, the solution calms down for a quiescent period during which the recorder indicates very slow evolution. The sudden foaming can hardly be due to a nucleation after gross supersaturation, for we have confirmed Morgan's[2] observation that bubbles of gas form and rise slowly even during a quiescent period. The foaming must be a consequence of a rapidly accelerated chemical reaction.

Behavior like that in Figure 1 is rather critically dependent upon the stirring conditions. In unstirred or very slightly stirred solutions, bursts of gas evolution are erratic. In rapidly stirred solutions, gas is evolved smoothly without periodicities.

Because of the difficulties of finding proper stirring conditions, we made only very rough measurements of compositions for which oscillations were possible. They were observed in a solution calculated to contain 20.2% HCOOH + 3.4% H_2O and in one containing 14.5% HCOOH + 6.6% H_2O. (Of course the remaining material was H_2SO_4 in both cases.)
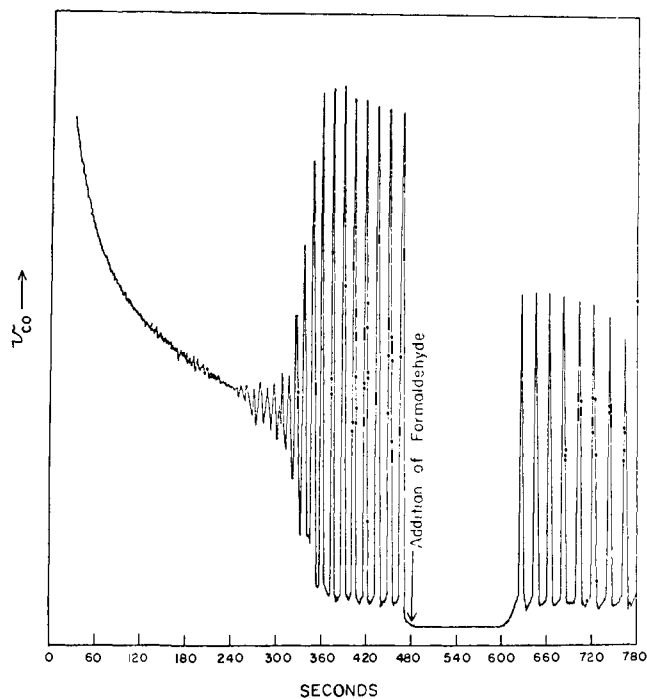
Figure 2. Rate of carbon monoxide production (in arbitrary units) at 55 °C by a stirred solution prepared from 4.0 mL of 88% aqueous formic acid and 10.0 mL of concentrated (ca. 97%) sulfuric acid. An addition of 0.3 mL of 37% aqueous formaldehyde was made at the time indicated. (Reprinted from *Acc. Chem. Res.*, **10**, 273 (1977).)

Kinetics of Smooth Decomposition. No oscillations were observed in systems that were stirred rapidly, but even these solutions exhibit kinetic anomalies that support our claim that the reaction is not a simple acidic catalysis.

Thus Ropp[6] at temperatures of 25 °C and less observed an induction period of the order of minutes that was larger at low temperatures and that could not be explained either by the time necessary to mix the solutions or to saturate the medium with carbon monoxide. He also asserted that the kinetics deviated from simple first order in substrate as the end of reaction approached.

At our higher temperature, the induction period could not be observed with certainty. However, during the first 5–10 min of reaction plots of ln v_{CO} were concave up indicating that the rate of CO formation decreased more rapidly than would be expected for a simple first-order reaction. At subsequent times, the ln v_{CO} plots exhibited excellent linearity indicating first-order kinetics with a rate constant of about 1.5×10^{-3} s^{-1}. This rate constant depends upon acidity of the medium as previously noted,[4] but it seems to be independent of stirring rate above the threshold for smooth decomposition. We are not prepared to explain these anomalies in detail, but a rationalization is suggested in the section on oxy nitrogen effects.

Products of Reaction. Not many gaseous products are conceivable from this system. We agree with all previous observers that CO is overwhelmingly the most important species. Our efforts to discover CO_2 by absorption in alkaline solution established only that this species was less than 2×10^{-5} mole fraction. Subsequent mass spectrometric measurements did indeed indicate a little CO_2 not ascribable to air contamination, but the amount from a typical run was 1.5×10^{-5} mole fraction of the CO. A run that was also 3.14×10^{-2} M in HNO_3 indicated 4.3×10^{-4} mole fraction CO_2, and a run 2.16×10^{-2} M in ferric ion indicated 3.7×10^{-4} mole fraction. This latter run was contaminated with several percent of air, and the accuracy of the measurement was poor. Therefore, our measurements indicate that CO_2 is always less than 0.1% of CO

and is only a little more than 0.001% if no additives are present. The products of eq 2 are truly negligible in importance.

Mass spectrometric measurements indicated no O_2 that could not be accounted for by air contamination as indicated by the Ar/O_2 ratio.

One other conceivable gaseous product is SO_2. The mass spectra gave no indication whatsoever of sulfur compounds. Our chemical tests based on iodine reduced no more than 5×10^{-6} mole fraction of SO_2 and gave no positive indication of even this amount.

Effects of Formaldehyde Addition. This study was undertaken with the frank prejudice[7] that radical (or triplet) species would be essential to the mechanism of any chemical oscillator. As part of a search for scavenger effects, we tried addition of formaldehyde to an oscillating solution. The dramatic results are shown in Figure 2.

After such an addition, evolution of gas could not be observed during an inhibition period of finite duration. The recorder trace demonstrates that gas evolution during the quiescent period of an oscillation is appreciably more than during the inhibition period after formaldehyde addition. After the inhibition period, a solution did not always resume oscillations, but it did resume gas evolution at a rate comparable to that during a quiescent period before the addition.

The formaldehyde inhibition period increased with increasing stirring rate and was too short to be detectable at the slowest stirring rate examined. The inhibition period was longer when formaldehyde addition took place later in a reaction so that less formic acid remained.

In one series of 14 experiments made as similar as possible, oscillating solutions were made from 0.8 to 2.2 M in formaldehyde, all additions taking place 7.0 min after the initial mixing of reagents. Inhibition periods ranged from 105 to 1247 s, increasing with increasing amount of added formaldehyde. The observations suggested that inhibition persisted until formaldehyde concentration had decayed to a certain critical value. A test was developed by the Guggenheim[8] method for treating first-order reactions with unknown infinity composition. Let F_t and $F_{t+\tau}$ be initial formaldehyde concentrations that generate inhibition periods of t and of $t + \tau$, respectively. For any selected τ, a plot of ln $(F_{t+\tau} - F_t)$ against t should give a straight line with slope equal to the first-order rate constant for decay of formaldehyde. At least for inhibition periods longer than 200 s, the data exhibited excellent linearity with a rate constant of 1.76×10^{-3} s^{-1}. We believe that it is coincidental that this rate constant for formaldehyde destruction differs by less than 20% from that for smooth decomposition of formic acid in a stirred medium.

Effects of Other Organic Additives. In view of these formaldehyde effects, it is perhaps remarkable that we observed no inhibition of oscillations from addition of solid trioxane, the cyclic trimer of formaldehyde. However, if trioxane was dissolved in a little water and then added, it inhibited oscillations as formaldehyde did. Whenever we used formaldehyde to inhibit oscillations, a small amount of white solid condensed in the cooler parts of the apparatus. We thought that this solid might be trioxane but did not conduct any tests for that hypothesis.

Additions of methanol, ethanol, and acetone also caused inhibition periods, but the effects were not as dramatic as with formaldehyde. Acrylamide is a frequently used radical scavenger that slowed the rate of CO evolution by an amount suggesting that it is two or three times as efficient as formic acid at reacting with radicals, but inhibition was not nearly as effective as that by formaldehyde. We can rationalize the difference by noting that radicals formed by hydroxyl radical addition to acrylamide could still conceivably oxidize ferrous ion or abstract hydrogen from protonated formic acid, while the HCO radicals derived from formaldehyde could not.

Effects of Iron Salts. Iron salts (apparently mostly in the ferric state) are ubiquitous impurities in these reagents. Spectrophotometric analyses with thiocyanate indicated that our formic acid contained enough ferric ion to make a typical reaction mixture about 8×10^{-6} M (including about 1 ppm in the sulfuric acid). We attempted to reduce this iron impurity by distilling the formic acid twice and by using Ultrex sulfuric acid claimed to have only 3 ppb of iron. If our distillation was effective at removing iron from the formic acid, we reduced iron concentrations to 7×10^{-8} M but still had oscillations. (Because iron is leached from glass, it is difficult to be sure about these low concentration limits.)

Other tests consisted of adding iron salts such as ferric sulfate or hydrated ferrous sulfate to the formic acid. Increasing ferric concentration to 4×10^{-3} M caused only about a 10% increase in the rate constant for smooth decomposition in a stirred solution, and oscillations were observed at ferric concentrations up to 2×10^{-2} M. Qualitative impressions indicated a synergesic effect between iron and nitrate. One solution about 3×10^{-2} M in nitric acid and 1×10^{-5} M in ferric ion oscillated particularly effectively with little influence by stirring rate. Admittedly these observations do not unequivocally implicate iron salts in the mechanism, but our impressions of such implication were definite.

Effects of Nitrates. Morgan[2] commented, "Nitric acid completely changed the whole nature of the action." He reported enhanced gas evolution and a blue color (perhaps N_2O_3) that came and went. In our experiments, nitrate was supposedly present at 0.2 ppm even in the Ultrex sulfuric acid. Effects we observed from small additions were often subtle but suggested that oxy nitrogen chemistry could significantly affect the oscillations. Thus, added KNO_3 appreciably shortened the inhibition period due to formaldehyde addition.

The chemistry of oxy nitrogen reactions with formic acid can be complex. Pollard and Holbrook[9] studied the gas phase reaction $HCOOH + NO_2 \rightarrow CO_2 + NO + H_2O$ and reported it to be heterogeneous and autocatalytic with the rate increased by the product NO. Barton and Yankwich[10] confirmed this observation and examined isotope effects in the reaction. We observed a solution analogue involving extreme autocatalysis. A mixture of formic and concentrated nitric acids sat quietly for several minutes while it became more and more brown with NO_2. Then bubbles began to form, and a few seconds later the whole solution erupted vigorously. *Extreme precautions are recommended for persons attempting to repeat this observation.*

Effects of Hydrogen Peroxide. When 1.0 mL of 30% H_2O_2 was added to a typical 14-mL oscillating system, the oscillations ceased and the infrared spectrum of the evolved gas indicated only CO_2 with no CO. Addition of only 0.1 mL of hydrogen peroxide did not suppress oscillations, but the spectrum revealed both CO and CO_2.

In two experiments in which 2.12×10^{-3} mol of H_2O_2 was added to a typical reaction solution (containing 0.095 mol of HCOOH), the amount of CO_2 produced was about one-fifth of that expected from the stoichiometry

$$H_2O_2 + HCOOH \rightarrow CO_2 + 2H_2O \qquad (3)$$

No gaseous product formed when either 1.0 or 10.0 mL of 30% H_2O_2 was added to 4.0 mL of 88% HCOOH, but addition of 10.0 mL of 97.2% H_2SO_4 to the second mixture generated a large quantity of CO_2 with a smaller amount of CO.

These experiments indicate that hydrogen peroxide oxidizes formic acid only in strongly acid solution, that the reaction is not quantitative (presumably because disproportionation to oxygen and water takes place simultaneously), and that the reaction producing carbon monoxide is at least partly inhibited by the presence of hydrogen peroxide.
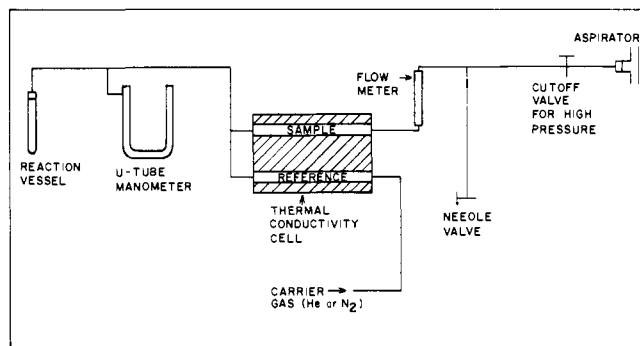

Figure 3. Schematic representation of the apparatus used for experiments in which the carbon monoxide pressure above the reaction mixture was maintained below or above atmospheric pressure. The aspirator was used to lower the pressure to a constant value determined by the valve setting. For the high-pressure experiments, the carrier gas was used to pressurize the system. The valve to the aspirator was closed and a constant pressure was maintained with the needle valve.

Effects of Changing Gas Pressure. By use of either a needle value or an aspirator, the pressure of gas in the system could be varied between about 100 Torr and 3 atm. A rough diagram of the arrangement is shown in Figure 3. Regardless of the total pressure in the system, the gas in contact with the reactant solution was almost pure CO.

Our experiments indicated a critical pressure of about 200–300 Torr below which we were unable to adjust a stirring rate such that oscillations occurred. If there is a high pressure limit for oscillations, it is above 3 atm.

If solutions were stirred rapidly enough to ensure smooth decomposition, the first-order rate constant for consumption of formic acid increased by a factor of only 1.3 when the pressure was increased from 0.07 to 3.03 atm.

One mixture that had been generated with distilled formic acid was brought to oscillation at about 1.8 atm, and the pressure was reduced to 1.0 atm in increments without changing the stirring rate. The period of oscillation went from about 12 to about 5 s along a smooth curve during this reduction of pressure.

Some of the most interesting pressure experiments involved bringing the system to apparent equilibrium at 3 atm. When no more gas evolution was detectable, the pressure was reduced to about 1 atm. At 1.00 atm, small periodic bursts of gas were then observed. At 1.01 atm, the bursts were still smaller and gave more rounded peaks on the recorder. At 1.02 atm and above, no gas could be detected. Some implications of these experiments are discussed in the section on onset of oscillations.

Effects of Other Variables. The experiments described above provided information significant to the mechanism developed below. We quote here a few other observations of less certain significance that may later contribute to our understanding in unforeseen ways.

The oscillations were unaffected by wrapping the reaction flask to exclude the light in the room.

When solid Na_2SO_3 was added, oscillations stopped until SO_2 had all been evolved; then they began again.

When methanesulfonic acid–phosphorus pentoxide[11] was used instead of sulfuric acid, smooth gas evolution occurred but no oscillations could be generated. When formaldehyde was added to such a reaction mixture, evolution of gas was quenched.

Development of Mechanism

General Principles. The preceding section has summarized a considerable body of experimental observations. A coherent mechanistic explanation should be possible in terms of elementary processes that take place in a single step or that involve

transient intermediates always present in very low concentrations and impossible to divert to more than a single set of products. As has been pointed out elsewhere[12] the direction of reaction of such elementary processes is determined strictly by thermodynamics even in the most complicated chemical systems. As we have done when elucidating the mechanisms of other oscillators,[13,14] we shall start with stoichiometric and thermodynamic restrictions and shall build our case to emphasize the probability that our conclusions are almost unique as explanations of the data.

Permissible Species. The reaction generates carbon monoxide in repetitive bursts, yet gas bubbles can be seen during quiescent periods of slow gas evolution between bursts. Therefore, the bursts are due to rapid onset of chemical reaction and are not due to relief of supersaturation by sudden nucleation of bubbles.

Sufficiently rapid stirring can prevent the bursts and convert the system to smooth gas evolution. Therefore, the carbon monoxide product is chemically involved and can autocatalytically promote its own formation if it is not removed sufficiently rapidly. We cannot imagine any rapid reversible chemical reaction of carbon monoxide except as a ligand with transition metal ions. The most important metallic impurities in commerical sulfuric acid are iron, copper, nickel, and lead. We have somewhat arbitrarily selected iron salts to use for the following explanation. Our observations of effects of additions of ferric sulfate are inconclusive but are not inconsistent with this interpretation.

Nitrates are also present as impurities in sulfuric acid. For reasons discussed below, we have tentatively omitted them from our proposed mechanism but recognize that that decision may have to be revised.

Small additions of species like formaldehyde can profoundly but temporarily affect the reaction. Such additions could not conceivably affect the acidity of concentrated sulfuric acid and especially could not do so reversibly. We therefore reject the previous view that the reaction results primarily from direct acid catalysis, although a small amount of such a reaction remains possible.
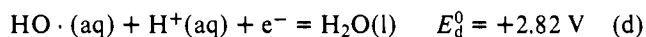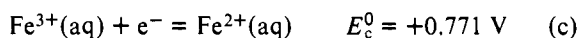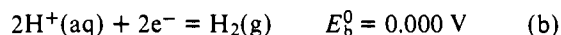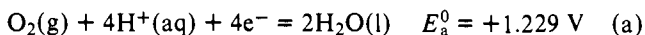
We failed completely in all efforts to detect sulfur dioxide or other sulfur compounds in the evolved gas. We conclude that sulfuric acid is a strongly acidic dehydrating agent but is not chemically reactive in this system.

We can devise no formic acid reactions maintaining paired electrons (except proton transfers already rejected) sufficiently rapid to explain the sudden bursts of chemical reaction. We conclude that the important mechanism is free radical, and the effects of additives are consistent with this interpretation.

If the mechanism involved the reducing radicals H· and HĊO, the product gas should have significant H_2. We could not have detected this species with our mass spectrometer. However, H_2 could form only if oxidized species also formed, and the only conceivable candidates are CO_2 and O_2; neither was detected in significant amounts.

The method of Holmes[15] drives us to implicate the oxidizing radicals, of which the only plausible candidates are HO·, H_2O^+·, SO_4^-·, HSO_4·, and $H_2SO_4^+$·. Rapid proton and hydrogen atom transfer will maintain all five of these species in rapid equilibrium, so we shall lose no generality if we ignore those radicals derived from sulfuric acid. The subsequent discussion will use HO· and H_2O^+· as permissible intermediates, recognizing that they are in rapid equilibrium in this acidic medium.

Thermodynamic Constraints. If formic acid is temporarily ignored, the species selected as significant generate four independent reduction potentials[16] in dilute aqueous solution.

$$O_2(g) + 4H^+(aq) + 4e^- = 2H_2O(l) \qquad E_a^0 = +1.229 \text{ V} \qquad (a)$$

$$2H^+(aq) + 2e^- = H_2(g) \qquad E_b^0 = 0.000 \text{ V} \qquad (b)$$

$$Fe^{3+}(aq) + e^- = Fe^{2+}(aq) \qquad E_c^0 = +0.771 \text{ V} \qquad (c)$$

$$HO \cdot (aq) + H^+(aq) + e^- = H_2O(l) \qquad E_d^0 = +2.82 \text{ V} \qquad (d)$$

If these four half-reactions are brought to simultaneous equilibrium in dilute aqueous solution saturated with oxygen at 0.20 atm, the composition is given by the equations

$$[HO \cdot] = 1.86 \times 10^{-27} \text{ M} \qquad (4)$$

$$[Fe^{3+}]/[Fe^{2+}] = 3.69 \times 10^7[H^+] \qquad (5)$$

$$P_{H_2} = 6.30 \times 10^{-42} \text{ atm} \qquad (6)$$

These equilibrium compositions correspond to about one HO· radical per cubic meter of water and to less than one H_2 molecule per 10^6 km³ of gas! Even in 1 M acid, less than one in 10^6 iron ions is in the +2 oxidation state, and the fraction will be very much less in strong sulfuric acid.

These calculations were made for dilute aqueous solution with water defined as unit activity. In a medium of 94% H_2SO_4 and 6% H_2O, the activity of water[17] might be as small as 10^{-5}, and the activity coefficient of HO· should be less than unity but probably not as small as the activity coefficient of water. We conclude that the concentration in eq 4 is an *upper* limit for the equilibrium concentration in sulfuric acid saturated with air. It is utterly inconceivable that hydroxyl radicals in that concentration could attack formic acid with an effective rate constant of the order of 10^{-3} s^{-1}.

These equilibrium calculations were for solutions containing no formic acid. The reduction potential involving this species is E_e^0.

$$HO \cdot (aq) + H^+(aq) + CO(g) + e^- = HCOOH(aq)$$
$$E_e^0 = +2.64 \text{ V} \qquad (e)$$
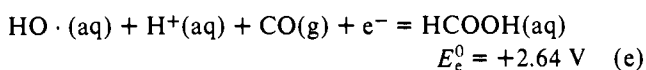
In 1 M aqueous formic acid saturated with CO, the concentration of hydroxyl radicals might be about 10^3 times as large as in water alone; the difference has no significant effect on the conclusion of the preceding paragraph.

Interaction of Kinetic and Thermodynamic Factors. No chemical system can oscillate unless it is far enough from equilibrium.[18] Therefore, some of the potential equilibration reactions must be slow. Thus half-reaction (a) involves breaking the strong bond in oxygen and will not couple at a significant rate with any of the other half-reactions.

Half-reaction (b) seems only somewhat better. Any H_2 in the system is being constantly swept out of solution by evolving gas, and $H_2 + 2HO· \rightarrow 2H_2O$ can hardly have much influence on the population of hydroxyl radicals. The reaction $2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2$ may indeed be the most important way that the [Fe(III)]/[Fe(II)] ratio is changed. We have not made any kinetic measurements but anticipate that it would be second order in Fe(II) and slow when Fe(III) is in large excess.

It is well known that hydroxyl radicals react very rapidly with ferrous ions[19] and we would expect half-reactions (c) and (d) to couple effectively to establish equilibrium. Even if they are only present in parts per million, the total concentration of iron salts will be very much greater than that of hydroxyl radical, and iron salts will serve as a buffer for radical concentrations. Therefore, *the instantaneous [Fe(III)]/[Fe(II)] ratio and the instantaneous reduction potential of Fe(III) will uniquely define the hydroxyl radical concentration at any moment.*

Let E_{Fe}^0 be the reduction potential for the half-reaction Fe(III) + e$^-$ = Fe(II). It will be a function of the ligands with which the iron is complexed. This half-reaction can be combined with (d) to give

$$[HO \cdot] = \frac{[Fe(III)]a_{H_2O}}{[Fe(II)][H^+]\gamma_{HO \cdot}} \exp[E^Q_{Fe} - 2.8)F/RT] \quad (7)$$

In this equation, a_{H_2O} is the activity of water defined to be unity in pure liquid, and $\gamma_{HO \cdot}$ is the activity coefficient of hydroxyl radical defined to be unity in dilute aqueous solution. Activity coefficients of iron salts and of hydrogen ion are incorporated into the definition of E^Q_{Fe} for convenience. As the preceding section showed, if $E^Q_{Fe} = E^Q_c$, then eq 7 indicates an utterly inconsequential concentration of hydroxyl radicals if a single iron(II) ion exists in 1 L of solution. Only a dramatic change in E^Q_{Fe} would permit a kinetically significant concentration of hydroxyl radicals to develop.

Effects of Ligands on Hydroxyl Radical Concentrations. Water molecules and sulfate ions generate weak crystal fields, and iron(II) and -(III) ions complexed with them have four or five unpaired electrons, respectively. The species CO, CN^-, and NO^+ are isoelectronic ligands exerting strong crystal fields and interacting particularly with filled d orbitals; iron(II) and -(III) ions complexed with them have zero or one unpaired electron, respectively.

Complexation with these ligands particularly stabilizes the iron(II) state and makes iron(III) a much stronger oxidizing agent. Although $Fe(CN)_6^{3-}$ ($E^Q_{Fe} = 0.36$ V) is a somewhat weaker oxidizing agent than $Fe(OH_2)_6^{3+}$ ($E^Q_{Fe} = 0.771$ V), it is surprising that a -3 charged ion is at all comparable to a $+3$ ion in the same oxidation state. Some more relevant reduction potentials are taken from a recent paper by Toma and Creutz:[20]

$$Fe(CN)_5OH_2^{2-} \quad E^Q_{Fe} = 0.39 \text{ V}$$

$$Fe(CN)_5CO^{2-} \quad E^Q_{Fe} = 1.18 \text{ V}$$

$$Fe(CN)_5NO^- \quad E^Q_{Fe} > 1.2 \text{ V}$$

If substitution of a single water molecule by CO can increase a reduction potential by 0.8 V, the redox chemistry of iron salt solutions can be profoundly altered by carbon monoxide saturation.

As reported above, formic acid in a well-stirred solution undergoes decarbonylation with an effective first-order rate constant of about 1.5×10^{-3} s^{-1}. Radiation chemical studies[21] indicate that the rate constant for hydroxyl radical attack on formic acid is 1.25×10^8 M^{-1} s^{-1} at pH 1. If these measurements at very different acidities can be compared, the hydroxyl radical concentration was about 10^{-11} M in the smooth decarbonylation studies. If $[Fe(III)]/[Fe(II)] = 10^4$ and if plausible values are assigned to the other quantities in eq 7, this concentration of HO· might be attained with $E^Q_{Fe} = 2.5$ V. If hydroxyl radical is formed more rapidly by oxidation of formic acid (reaction e) than of water (d), the critical E^Q_{Fe} is 2.3 V. Bursts like those observed with less stirring would require E^Q_{Fe} to become at least 0.1 V more positive than these minimum values. The large effect of substituting a single water molecule with CO in the pentacyano complex suggests that these large reduction potentials are possible at high concentrations of carbon monoxide.

A Possible Mechanism for Oscillations. These ideas permit us to rationalize an oscillator mechanism that seems consistent with previously established mechanisms.[7,13,14]
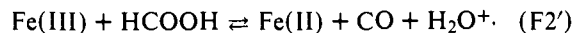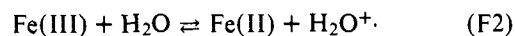
An initial solution of formic acid in concentrated sulfuric would have negligible radical content but could react slowly by the step

$$HCOOH + H^+ \rightarrow CO + H_2O + H^+ \quad (F1)$$
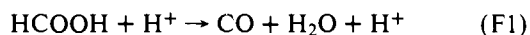
This acid-catalyzed reaction would involve a *proton* transfer from the carbon of formic acid and would presumably be a concerted process passing through transition state structure I.


(I)
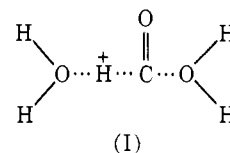
The medium contains iron salts mostly in the ferric form. They could be reduced by the reversible reactions

$$Fe(III) + H_2O \rightleftharpoons Fe(II) + H_2O^+ \cdot \quad (F2)$$

$$Fe(III) + HCOOH \rightleftharpoons Fe(II) + CO + H_2O^+ \cdot \quad (F2')$$

involving water and formic acid as reductants. Of course $H_2O^+ \cdot$ is a protonated hydroxyl radical. Equation 5 predicts that $[Fe(III)]/[Fe(II)]$ is about 10^{15} for a solution in equilibrium with atmospheric oxygen in about 90% sulfuric acid having a Hammett[22] H_0 of about -8. As CO accumulates owing to formic acid decomposition, E^Q_{Fe} will increase and shift these equilibria to the right with increase in hydroxyl radical concentration.

Hydroxyl radical will catalyze the decomposition of protonated formic acid by the step

$$HO \cdot + HCOOH_2^+ \rightarrow H_2O + CO + H_2O^+ \cdot \quad (F3)$$
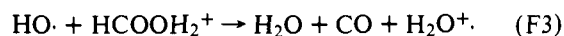
We regard this step as a concerted *hydrogen atom* transfer passing through transition state structure II. If it were not

(II)
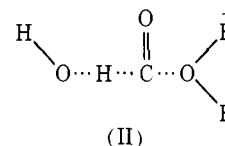
concerted, the radical OĊOH would be produced, and we believe that this may happen at lower acidities. Gordon and Ausloos[23] estimate gas-phase bond dissociation enthalpies for this radical as 1 kcal/mol for the O–H bond and 26 kcal/mol for the C–O bond. If this radical forms as an intermediate, the products would favor CO_2 rather than the observed CO. Further support for the reaction being concerted is provided by studies of Hart et al.[24] on the radiation chemistry of aqueous formic acid. They found that CO was favored over CO_2 as the system was made more acidic just as is predicted if hydrogen atom transfer from the protonated acid is concerted and accompanied by CO formation.

Step F3 produces carbon monoxide which shifts the equilibrium of step F2 to the right producing more hydroxyl radical. Therefore, step F3 contains provision for autocatalysis just as in other oscillator mechanisms.[7]

If the mechanism is to resemble the Oregonator[25] model, hydroxyl radical should behave as a switched intermediate that is destroyed by both first- and second-order processes. Reactions $-F2$ and $-F2'$ are both first order in radical and do not shift the $[Fe(III)]/[Fe(II)]$ equilibrium. A referee has pointed out that hydroxyl radicals are also destroyed by the step

$$CO + HO \cdot \rightarrow CO_2 + H \cdot \quad (F4)$$
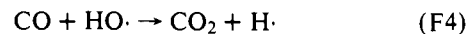
Hart et al.[27] report a rate constant of 4.5×10^8 M^{-1} s^{-1} in aqueous solution. This constant is comparable to that for F3,[21] but relative concentrations of HCOOH and of CO make step F3 at least 100 times as fast as F4. If the hydrogen atoms combine with other radicals or reduce Fe(III), step F4 is chain terminating; if those hydrogen atoms attack formic acid in an analogue of F3, the chain continues but a small fraction of the decomposition products corresponds to reaction 2 instead of reaction 1. We are not yet prepared to say which interpretation conforms better to our observations.

A reasonable second-order termination step is

$$2HO \cdot \rightarrow H_2O_2 \quad (F5)$$

Whenever it occurs, two radicals are destroyed. Those radicals were formed by steps F2 or F2', so the net effect of F5 is to increase the concentration of Fe(II). As [Fe(II)] increases, eq 7 shows that the concentration of radicals will decrease, and the burst of CO formation will subside. Carbon monoxide will then escape from the solution, and E_{Fe}^0 will become less positive and still further reduce radical concentrations.

Another burst of chemical reactivity must await processes that remove the Fe(II) and H_2O_2 resulting from radical termination step F5. The easiest way to accomplish this change is by the step

$$Fe(II) + H_2O_2 + H^+ \rightarrow Fe(III) + HO\cdot + H_2O \quad (F6)$$
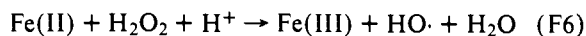
This process is well known and rapid[19] in solutions without carbon monoxide. It will be thermodynamically allowed only if enough carbon monoxide has escaped to reduce E_{Fe}^0 below the value it has at the time of greatest chemical reaction.

Instead of step F6, the hydrogen peroxide might be destroyed by formic acid by reaction 3. We find that this reaction takes place only in strong acid and might be a *hydride ion* transfer to protonated hydrogen peroxide by transition state structure III. If hydrogen peroxide reacts in this way, Fe(II)

(III)
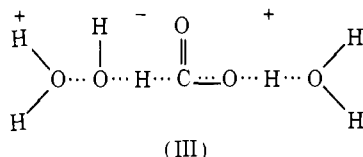
is presumably regenerated by the net reaction

$$2Fe(II) + 2H^+ \rightarrow 2Fe(III) + H_2 \quad (8)$$
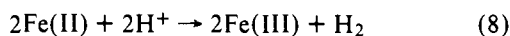
which could only take place after E_{Fe}^0 has fallen considerably as a result of loss of carbon monoxide. We are not yet in a position to say whether kinetic information favors restoration of the system by step F6, which is the simplest possibility, or by reactions 3 and 8, which generate the products or eq 2 instead of those of eq 1.

Rationalization of Formaldehyde Effects. We can only explain our dramatic formaldehyde effects by proposing that this species scavenges hydroxyl radicals efficiently and that the resulting HCO radicals are inert to further chain propagation. Inhibition of formic acid decomposition persists until this additive has been irreversibly destroyed or volatilized from the hot solution.

Rationalization of Acidity Effects. The mechanism as developed above explains why oscillations could occur in solutions that were weakly stirred but could be suppressed if the stirring rate were sufficient to prevent E_{Fe}^0 from rising to the point at which hydroxyl radical concentrations increased autocatalytically. It should also accommodate the observation[4] that the rate in stirred solution is proportional to the Hammett H_0 function. Step F3 is a concerted process requiring protonated formic acid, and the pK of $HCOOH_2^+$ is estimated[26] to be -8.7 or more negative than the probable H_0 of the system. An appreciable fraction but still much less than one-half of the formic acid would be protonated, and the rate of a reaction of the protonated species should be proportional to H_0 just as is observed.

Relationship to Other Decarbonylation Reactions. It has generally been believed that decarbonylations of carboxylic acids are acid-catalyzed reactions. We now propose a hydroxyl radical mechanism for the reaction of formic acid. Radicals usually react with organic compounds either to add to multiple bonds or to abstract single atoms. We would not expect hydroxyl radicals to attack $RCOOH_2^+$ to form $ROH + CO$ if R were a conventional alkyl group. Decarbonylation of an RCO^+ species and solvation of the resulting carbonium species appears more plausible for most acids than does the special

formic acid radical mechanism. However, it is possible to devise plausible radical mechanisms for the decomposition of oxalic acid by the net reaction $HOOCCOOH \rightarrow CO_2 + CO + H_2O$.

Possible Oxy Nitrogen Effects. We presented evidence that nitrates could strongly influence formic acid reactions, but we did not invoke any nitrogen chemistry in the mechanism as developed. As we also pointed out, the nitrosonium ion NO^+ is a strong crystal field ligand that can greatly increase the reduction potential of Fe(III). Nitrates could certainly promote reaction in this way after they had been reduced to N(III). However, N_2, N_2O, NO, and NO_2 are all gaseous species that would be swept from a solution foaming with evolved gas. Even though NO^+ could augment reactivity, it could not eliminate the need to invoke iron salts in the mechanism. We have tried to develop our mechanism without invoking oxy nitrogen species that we would expect to be supplementary and transient. Our observation of enhanced rates during the first few minutes could be rationalized if acceleration by nitrosonium did indeed occur until oxy nitrogen species had been swept out. Such an interpretation is pure speculation.

Point of Onset of Oscillations. It is well established that oscillations are impossible in a system sufficiently close to equilibrium.[18] As the system is displaced from equilibrium, a bifurcation point may be reached beyond which oscillations become possible. Mathematical theories are still inexact at predicting the distance from equilibrium at which oscillations would become possible. The experimental observations we have made of pressure effects suggest that oscillations begin when the free energy of the system is displaced from equilibrium by $RT \ln 3$ per mol of formic acid. Not many oscillatory systems lend themselves to this sort of quantitative measurement, and we believe that further studies of this nature would be useful to developing the theory of oscillators.

Caveat. We have proposed a complicated mechanism to explain a considerable body of rather unusual chemistry. The final criterion for such a mechanism must be its consistency with the full body of experimental fact. Although we feel encouraged by the range of observations that can be accommodated to the mechanism as developed here, a few points rouse various degrees of concern. We cite some examples:

(a) Strongly stirred solutions undergo smooth decomposition that appears to be almost independent of pressure over a considerable range both above and below 1 atm. A related observation is the independence of decomposition rate on stirring rate as long as stirring is rapid enough to prevent oscillations. Our explanation would seem to require that E_{Fe}^0 is almost independent of carbon monoxide concentration over a rather wide range near saturation at 1 atm but that this reduction potential increases dramatically for somewhat higher carbon monoxide concentrations. Such rationalization is conceivable but uncomcomfortably ad hoc.

(b) Figures 1 and 2 both show that the initial decomposition reaction is smooth until much of the formic acid is gone, and oscillations develop somewhat gradually with increasing amplitude. At high acidities, the Bray reaction behaves the same way,[14] and oscillations begin only after most of the initial hydrogen peroxide is gone. On the other hand, the Bray reaction at low acidities[14] and the Belousov–Zhabotinsky reaction[13] jump immediately to full amplitude oscillations once the induction period is over. We are not yet sure that our mechanisms can model these differences in the onset of oscillations.

(c) We could not detect any evolved oxygen that could not be accounted for by a few percent of air contamination as indicated by argon pressure. Our mechanism terminates bursts of gas evolution by forming hydrogen peroxide under conditions of high hydroxyl radical concentration. We would certainly expect O_2 molecules to form under such conditions, but it may be that the periods of intense activity can be terminated

by forming such small amounts of iron(II) that our analytical methods cannot identify the oxygen derived from the equivalent amounts of hydrogen peroxide.

(d) The mechanism as developed here suggests that the oscillations could be followed potentiometrically. We made a number of experiments in which we recorded the potential between a platinum and a glass electrode. Tantalizing suggestions of oscillations could never be surely separated from noise due to bubbles on the electrode surface. We observed only small potential differences between sulfuric acid solutions prepared entirely with ferric or with ferrous salts. It appears that in this highly acidic medium the metal surface is so swamped by interaction with protons that small amounts of metal ions have no significant effect on the potential.

The above observations cause us a little concern as to whether we have yet identified all of the essential features of the mechanism. However, we have demonstrated unequivocally that oscillations do occur, that bursts of gas evolution do not result from nucleation of a supersaturated solution free of any gas phase, and that carbon monoxide therefore reacts chemically to promote its further formation. The mechanism we have developed does accommodate these facts, and we are unable to devise any alternative scheme that does not involve carbonyl complexes of transition metal ions. We hope that the essential features will stand up to further scrutiny, and we propose to undertake model calculations to test the mechanism further.

pointing out the large effect of carbonylation on eduction potential of iron(III).

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Electronic Structure and Protonation of Alkyl Chlorides[1]

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Abstract: Trends and correlations for several properties of alkyl chlorides including ionization potentials, proton affinities and force constants are discussed using both experimental data and the results of MINDO/3 computations. The linear dependence of ionization potentials on Taft's σ^* constant appears to be valid only for simple, acyclic alkyl chlorides. However, a good, general correlation is discovered between proton affinities and the total charge on the ClH fragment in protonated alkyl chlorides. Thus, the ability of the alkyl group in RClH$^+$ to accommodate positive charge controls the proton affinities. This leads to the observation that there is a rough relationship between proton affinities and solvolysis rates. The utility of protonated chlorides as models for ion pairs is also considered. The stabilization of a carbonium ion by HCl in RClH$^+$ is found to be consistent with a simple charge transfer expression. Implications concerning the differential solvation of carbonium ions are discussed.

Alkyl halides are an important class of organic compounds owing to their widespread use as electrophilic substrates in carbon–carbon bond forming reactions, functional group interconversions, and solvolysis experiments.[3] Consequently, it is not surprising that some effort has been devoted to determining their physical characteristics, e.g., structural parameters,[4] ionization potentials,[5] electronic spectra,[6] dipole moments,[7] vibrational spectra and force constants,[8] dissociation energies,[9] conformational preferences,[10] and proton affinities.[11] The predominance of the data pertains to simple, acyclic compounds, which leaves a disappointing storage of quantitative information on the properties of cyclic alkyl halides.

Although understanding of these species could be enhanced, in principle, by studies employing nonempirical molecular orbital methods, such calculations have been generally restricted to simple fluorides owing to the large number of basis functions needed to describe the other halides.[12] Unfortunately, fluorides are less interesting from a traditional, experimental standpoint than chlorides, bromides, or iodides, since fluoride ion is both a relatively poor nucleophile and leaving group in protic solvents.[3]

An alternative for the study of these compounds is the semiempirical MO method, MINDO/3. Both Dewar[13] and we[2] have found the results to be in good agreement with ex-