Gas Evolution Oscillators. 1. Some New Experimental Examples[1]

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Abstract: We report for the first time that malic, oxalic, tartaric, citric, and malonic acids decompose in concentrated sulfuric acid with oscillatory evolution of oxides of carbon. We also report oscillatory gas evolution during the reactions of aqueous nitrous acid with both ammonium ion and urea. Some other gas evolution reactions did not exhibit oscillatory behavior in our hands, but oscillatory gas evolution is obviously a more common phenomenon than has previously been appreciated.

Over 60 years ago, Morgan[3] observed oscillatory evolution of carbon monoxide during the decomposition of formic acid in concentrated sulfuric acid. This was in fact the first oscillating chemical reaction discovered, predating the Bray–Liebhafsky[4] reaction by 5 years and the Belousov–Zhabotinsky[5] reaction by over 40 years.

Two recent independent studies of the Morgan reaction by the present authors and their co-workers led to very different explanations of the rhythmic gas evolution. Showalter and Noyes[6] invoked an elaborate chemical mechanism that involved iron salt impurities and was suggested by analogies with the oxidation–reduction oscillators that were already understood. In contrast, Bowers and Rawji[7] invoked a physical mechanism based on a supersaturation–desaturation cycle in which fractionation in the foam played a key role.

Our further independent studies led to discovery of two other examples of oscillatory gas evolution from aqueous solution. These reactions are the decomposition of benzene diazonium chloride[8] and the decomposition of hydrogen peroxide catalyzed by iron salts.[9] It is difficult to accommodate either of these reactions to the mechanisms previously proposed for the Morgan reaction. Thus, these aqueous solutions do not exhibit much foaming, and no plausible mechanism of either reaction could generate a purely chemical instability.

The present paper reports the observation of oscillatory gas evolution during a number of other chemical reactions. Subsequent papers (in *J. Phys. Chem.*) will report quantitative measurements of the Morgan reaction including parameters like critical supersaturation and will then develop a detailed explanation of gas evolution oscillators in terms of nucleation and bubble growth.

Experimental Details

Chemicals were reagent grade and used without further purification. Anhydrous oxalic acid was prepared by heating the monohydrate in a 100 °C oven. Triply distilled water was used to prepare solutions.

The reaction vessel was a large tube immersed in a thermostated water or glycerol bath. The tube was connected both to an adjustable capillary leak to the atmosphere and to a Celesco variable reluctance pressure transducer and transducer indicator. The output of the indicator was connected to a chart recorder. Rhythmic gas evolution gave rise to a waveform transducer output such as those in Figures 1, 2, and 4. In these diagrams, the *y* axis, which is labeled d(gas)/d*t*, is an uncalibrated

and only approximately linear measure of the rate of gas evolution, and the scale depends on the dimensions of the capillary. Integrated step-form curves (Figure 3) were obtained by replacing the capillary with a 2-L flask and measuring total gas pressure as a function of time. The linear recorder output was calibrated in separate experiments.

The nature of the product gases was determined by infrared absorbance with a Sargent-Welch 3-200 spectrophotometer and a 10-cm gas cell.

Results

Organic Acid Reactions. It is well-known that in concentrated sulfuric acid at elevated temperatures many carboxylic acids decompose with or without loss of water to produce carbon monoxide and/or dioxide. In Table I we report, apparently for the first time, oscillatory gas evolution during several of these decompositions. These reactions require more severe conditions than the formic acid reaction discovered by Morgan,[3] and most of them are less spectacular with only a few pulsed releases of gas. Representative traces of pressure vs. time are shown in Figures 1–3.

As in the case of the Morgan reaction, the frequency and amplitude of the pulses, or indeed their appearance at all, depend rather critically on temperature, starting concentration, and degree of agitation. Except for the Morgan reaction, which oscillates over a fairly wide range of conditions, the concentrations and temperatures shown in Table I are the minimum at which gas evolution was brisk enough to produce oscillations. Moderate magnetic stirring increased the amplitude and prolonged the oscillatory phase of the reactions.

In general these reactions pass through four stages, with the relative importance of each depending on the specific reaction and set of conditions. The first stage is an induction period with little or no gas evolution. It usually lasts less than 30 s and includes an initial time for mixing and dissolution in the viscous solvent. The induction period is followed by a burst of vigorous nonoscillatory gas production with the mixture foaming to several times its liquid volume. The third and oscillatory stage of each reaction begins as the vigorous evolution subsides. Figure 1 for citric acid and Figure 2b for oxalic acid show particularly clearly how the amplitude of the oscillations under some conditions builds up to a maximum through several cycles before dying away. In other cases the amplitude decreases steadily from the start. The reactions continue to equilibrium in a slow final stage which may last many hours and which is not visibly or detectably oscillatory.

The integrated gas evolution curves in Figure 3 contrast the sharpness of the oscillations in two cases and indicate the relative rates of gas evolution during rapid and slow portions of a cycle. Formic acid (Figure 3b) in the most favorable cases produces a "flat step" curve with gas release between the bursts being too small to show on the trace (although bubbles can still be observed visually). The other acids behave more like tartaric (Figure 3a), exhibiting a "slope step" curve with significant amounts of gas being evolved during the slow stage. The general appearance of the oscillations of all the acids is very similar to that which has

(1) Paper No. 51 in the series "Chemical Oscillations and Instabilities". No. 50: Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.*, **1982**, *86*, 5155.
(2) (a) University of Oregon. (b) Simmons College.
(3) Morgan, J. S. *J. Chem. Soc., Trans.* **1916**, *109*, 274–283.
(4) Bray, W. C. *J. Am. Chem. Soc.* **1921**, *43*, 1262–1267.
(5) Belousov, B. P. *Ref. Radiat. Med.* **1959**, *1958*, 145–147.
(6) Showalter, K.; Noyes, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 1042–1049.
(7) Bowers, P. G.; Rawji, G. *J. Phys. Chem.* **1977**, *81*, 1549–1551.
(8) Bowers, P. G.; Dick, Y. M. *J. Phys. Chem.* **1980**, *84*, 2498.
(9) Ganapathisubramanian, N.; Noyes, R. M. *J. Phys. Chem.* **1981**, *85*, 1103–1105.

Table I. Reactions Exhibiting Oscillatory Gas Evolution

reactants (initl conc, molal)	solvent[a]	temp, °C	period, s	max no. of oscillations	products	ref
malic acid (2.5)	A	85	10	>60	CO, trace CO_2	b
oxalic acid (3.5)	A	130	6	15	CO, CO_2	b
tartaric acid (2)	A	110	25-50	12	CO, CO_2, trace SO_2	b
citric acid (1.5)	A	90	20-40	20	CO, CO_2	b
malonic acid (3.3)	A	155	11-30	9	CO_2	b
formic acid (2.6)	A	45	30-50	>60	CO	3, 6, 7
formic acid (2.6), nitric acid (2.6)	A	50	30-40		CO, CO_2, NO_2	13
oxalic acid (3.7)	B	155	30-40	7	CO, CO_2	b
NH_4Cl (1.6), NO_2^- (2.5), H^+ (0.1)	C	31	12-15	25	N_2, NO, NO_2	b
urea (1.4), NO_2^- (4), H^+ (0.2)	C	27	30	7	CO_2, N_2, NO, NO_2	b
$C_6H_5N_2Cl$ (0.45)	C	60	8-10	>20	N_2	8
H_2O_2 (2.0), Fe^{3+} (0.07), H^+ (0.9)	C	37	~60	20	O_2	9

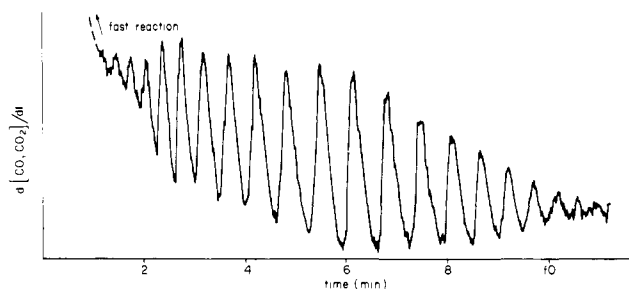[a] A ≡ 96% H_2SO_4; B ≡ 85% H_3PO_4; C ≡ H_2O. [b] This work.

Figure 1. Rate of gas release in arbitrary units for citric acid in sulfuric acid. Conditions are those in Table I.
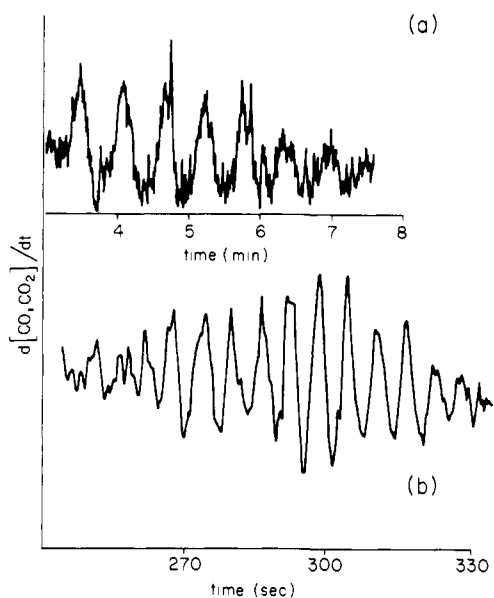

Figure 2. Rates of gas release in arbitrary units for oxalic acid in (a) phosphoric acid and (b) sulfuric acid. Conditions are those in Table I.

been described in detail for the formic acid case by Showalter and Noyes.[6]

Curves such as that in Figure 3 permit measurement of the change (Δc) in the concentration of dissolved gas that occurs during a single pulse. The maximum values for Δc (in units of 10^{-2} M pulse^{-1}) are as follows: formic, 7.5; tartaric, 3.7; citric, 15.0; malic, 5.6. Further measurements of this kind will be described in a later paper and constitute an important clue in elucidating a mechanism for the oscillations.

Nitrous Acid Reactions. Figure 4 shows the oscillatory release of nitrogen (with lesser amounts of nitrogen oxides) we observed upon treating aqueous solutions of NH_4Cl or urea with HNO_2. Both of these reactions show an induction period with almost no
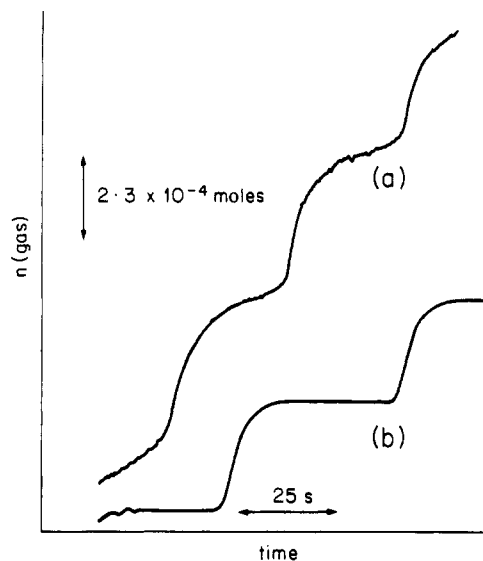

Figure 3. Portions of curves defining total gas evolved from (a) tartaric acid and (b) formic acid in concentrated sulfuric acid.
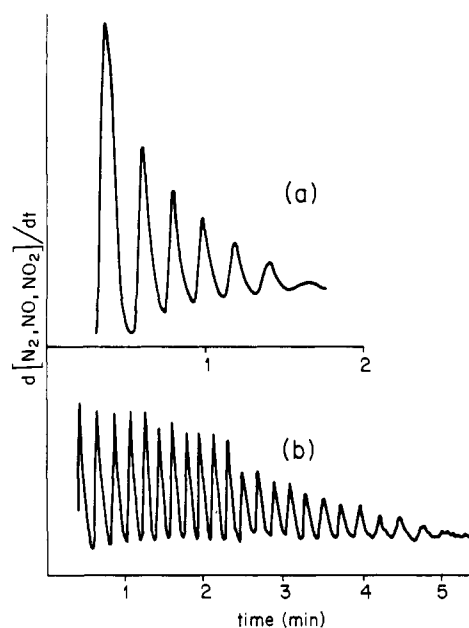

Figure 4. Rates of gas release in arbitrary units for reactions of HNO_2 with (a) urea (H_2NCONH_2) and (b) NH_4^+ in aqueous solution. Conditions are those in Table I.

Table II. Reactions Not Exhibiting Oscillatory Gas Evolution

first reactant	second reactant	solvent[a]	gaseous product
N_2H_4	Fe^{3+}, H^+	C	N_2
H_2NCONH_2	OBr^-	C	N_2
$NaBH_4$	H^+	C	H_2
NaCl	H_2SO_4	A	HCl
CO_3^{2-}	H^+	C	CO_2
SO_3^{2-}	H^+	C	SO_2

[a] A ≡ concentrated H_2SO_4; C ≡ water.

bubbles present followed by a chain of oscillations that (in contrast to the organic acid reactions) produce almost no foam.

If anything, oscillations in the two nitrous acid reactions are more irreproducible than those for the organic acids. Not only are concentration, temperature, and agitation important, but also pH and the order in which the reactants are mixed. At the conditions given in Table I, we found that the most repeatable oscillations were produced by mixing $NaNO_2$ and H_2SO_4 solutions and allowing the resulting HNO_2 solution to equilibrate to bath temperature (with occasional agitation to remove most of the NO_2 fumes) before being added to the NH_4Cl or urea.

Other Reactions. We tried without success to generate oscillations with a number of other reactions known to produce gaseous products. Some of these failures are summarized in Table II. Of course we have shown not that oscillatory gas evolution is impossible for these systems but only that such behavior was not exhibited in our hands.

Discussion

The main fact we wish to establish in this paper is that gas evolution oscillations are of much more widespread occurrence than has previously been reported. It is at first sight surprising that some of the oscillations have not been seen previously, because the overall kinetics of the reactions has been known for some years. This is particularly true for oxalic, citric, and malic acids[10] and for the HNO_2 processes.[11,12]

We believe there are two reasons oscillations were missed in earlier studies. In the first place, the concentrations required for rhythmic gas evolution (see Table I) are much higher than those that for obvious reasons were employed in regular kinetic studies. In the second place, measurements of gas evolution rates (a usual method for monitoring the reactions) are generally done with vigorous agitation to *prevent* supersaturation; while the oscillations, as we are now convinced, occur as a result of the natural release of supersaturation.

This first paper is intended to be primarily phenomenological with our interpretations to follow. However, it should already be apparent that we believe nucleation and supersaturation processes are the major factors responsible for oscillatory behavior in many of these systems. We do not exclude the possibility that chemical processes may sometimes couple with gas evolution in order to cause or enhance oscillatory behavior. The best candidates for such coupling with chemical reactions are the reactions of ammonium ion and urea with nitrous acid and the sulfuric–nitric–formic acid system of Raw et al.[13]

(10) Liler, M. "Reaction Mechanisms in Sulfuric Acid"; Academic Press: New York, 1971.

(11) Werner, E. A. "The Chemistry of Urea"; Longmans, Green & Co.: London, 1923.

(12) Hughes, E. D.; Ingold, C. K.; Ridd, J. H. *J. Chem. Soc.* **1958**, 58–65, 65–69, 70–76, 77–82, 82–88, 88–98.

(13) Raw, C. J. G.; Frierdich, J.; Perrino, F.; Jex, G. *J. Phys. Chem.* **1978**, *82*, 1952–1953.

(14) Degn, H. European Molecular Biology Organization workshop, Dortmund, Oct 1976.

Laser and Pulse Radiolytically Induced Colloidal Gold Formation in Water and in Water-in-Oil Microemulsions

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Abstract: Reduction of $HAuCl_4$ has been investigated pulse radiolytically in water and in water-in-oil microemulsions. Rate constants have been determined for $Au^{3+} + e_{aq}^- \rightarrow Au^{2+}$, $2Au^{2+} \rightarrow Au^{3+} + Au^+$, and $Au^+ + R^- \rightarrow Au^0 + R$ (where R^- is an unidentified radical). On the longer time scale formation of colloidal gold, $nAu^0 \rightarrow (Au^0)_n$, has been observed. Rate of colloidal gold formation has also been studied in the bombardment of $HAuCl_4$ solutions by 353-nm 60-mJ 3–5-ns laser pulses. Hydrodynamic diameters and polydispersities of empty and colloidal-gold-containing microemulsions have been determined by dynamic laser light scattering to be 150 and 220 Å, respectively. Morphologies of colloidal gold have been determined by electron micrography. There are a number of advantages of forming colloidal particles in microemulsions. Under identical conditions a greater amount of colloidal particles is formed than that in water. Colloidal gold particles formed in microemulsions are smaller and more uniform than those obtained in homogeneous solutions.

Introduction

Colloidal gold formation has been recognized for over 80 years.[3–5] Most methods of preparation involved the controlled

chemical reduction of chloroauric acid, $HAuCl_4$. The size of the particles (typically between 100 and 600 Å) and their distribution,

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(3) "Gmelins Handbuch der Anorganischen Chemie"; Verlag Chemie: GmbH, Weinheim/Bergstr., Germany, 1975; Vol. 62, Appendix 3, p 183.
(4) Papavassiliou, G. C. *Prog. Solid State Chem.* **1979**, *12*, 185.