# Corrosion of Iron by Ascorbic Acid and Catalysis of Ascorbate Oxidation by Products of the Iron Corrosion

A. Rosanoff,* George M. Briggs, and Benito O. de Lumen

Electrolytic iron (99.8% Fe) prepared as small plates was exposed to oxygenated solutions of ascorbic acid. Gravimetric corrosion rates and ascorbate oxidation rates were measured simultaneously in a new apparatus designed for that purpose. The mean corrosion rate was high for iron in 1 mM ascorbic acid at 365 mdd (mg $dm^{-2}$ $day^{-1}$) (6-h tests, $n = 12$) and was highly dependent upon ascorbate concentration, increasing to 3200 mdd in 11 mM ascorbic acid. Corrosion of iron in oxygenated, deionized water was zero for these tests. Ascorbic acid oxidation under these oxygenated conditions agreed well with the first-order rate model. Ascorbate oxidation proceeded slowly in the absence of iron. Mean $k_1$ (first-order rate constant) was increased 4–5 times by the presence of an elemental iron plate in the solution and 10 times by the addition of fine electrolytic iron powder (99.9% Fe). In these nonbuffered solutions, the ascorbate oxidation rate was unchanged when iron corrosion from plates was doubled or tripled in the solutions. High concentrations of iron powder in the solutions did not cause higher rates of ascorbate oxidation than small amounts of iron. Nutritional and food processing implications of these results are discussed.

Inadvertent addition of iron to foods via preparation in iron cookware has often been cited as being significant from a nutritional point of view (Walker and Arvidsson, 1953; Moore, 1965; Burroughs and Chan, 1972; Derman et al., 1980). However, the components of foods responsible for such corrosion have not been delineated. Other sources of iron contamination in foods have been reported. In a survey of 147 food manufacturing firms (Selby, 1954), it was found that the contaminants most frequently found in raw food materials and finished products were metal particles, predominantly iron. Such contamination comes from wear of machinery, especially grinding operations, worn plating, unsuitable joints, clips from belts, and loose nuts and bolts (Chatt, 1964). Cunningham and O'Brien (1972) developed a technique to determine the number of ferromagnetic particles that may be removed with a magnet from foods. Thirty-four out of sixty-one foods contained ferromagnetic particles up to 1.5 mm in length. Some of these particles were from fortification with iron powders. These and other studies (MacKay et al., 1945; Devadas et al., 1973; Rosanoff and Kennedy, 1982) clearly show that elemental iron is often a contaminant of foods with nutritional benefit.

It has been assumed that such iron contamination is detrimental to the vitamin C content of foods (Muneta, 1975), but in the extensive literature on causes of vitamin C degradation, no work appears to have been done that studied the effect of iron corrosion.

The corrosion rate of many metals in aqueous solutions can be dramatically increased by the addition of certain organic compounds to the solution, and ascorbic acid is one such compound (Massini, 1975). Since ferric ions catalyze the oxidation of ascorbic acid to dehydroascorbic acid in an autocatalytic reaction (Taqui-Khan and Martell, 1967; Sattar et al., 1977; Hegenauer et al., 1979), the corrosion of iron in ascorbic acid solutions may produce concentrations of ferric ions sufficient to catalyze the oxidation of ascorbic acid. This research project was designed to test this hypothesis and to determine the effect of ascorbic acid concentration on the corrosion rate of iron in an aerobic system.

Department of Nutritional Sciences, University of California, Berkeley, Berkeley, California 94720.

## MATERIALS AND METHODS

Thirty-five kinetic tests of the oxidation of 1.14 mM ascorbic acid (1.0 mg/5 mL) were performed at room temperature ($T$ = 22–25 °C) in glass corrosion cells described below. All tests were 4–6.0 h in length. Experimental solutions were unbuffered. pH was determined at the beginning of each test by using a Corning pH meter equipped with a calomel electrode. In 15 tests the oxygenated solutions were not exposed to any metal. In 14 tests one, two, or three plates measuring about 1 × 1 × 0.15 cm and formulated from electrolytic iron (described below) were suspended in the solution at time = 0. During these tests the gravimetric corrosion rates of each iron plate was determined. In six tests electrolytic iron powder (described below) was added to the ascorbic acid solutions at time = 0. In addition, the gravimetric corrosion rate of iron plates and the simultaneous ascorbic acid oxidation rate were determined for six concentrations of ascorbic acid of the range found in foods, from 0.12 to 11.6 mM.

**Corrosion Rate/Corrodent Chemistry Chambers (Cells).** All experiments were carried out in glass corrosion cells designed to measure the corrosion rate of metals simultaneously with chemical changes in the corroding solvent. Each cell consisted of a 1-L calibrated separatory funnel modified for continuous temperature measurement, for placement of a corrosion sample (plate), and for mixing the contents of the cell with oxygen gas (Figure 1).

Temperature was continuously monitored throughout all experiments from glass thermocouple wells that protruded from one side of the cell into the solution. These were fitted with copper–constantan thermocouples imbedded in glycerol and attached to a Leeds and Northrup multipoint temperature recorder. The corrosion cells were insulated with aluminized, vinyl foam pipe insulation that served to darken the cells's interiors as well as to maintain minimum heat exchange with the environment.

Between 900 and 1000 mL of ascorbic acid solution was routinely added to the chambers. In 14 tests, iron plates described below were suspended into the solution with size 50 cotton thread that was secured to a glass hook built into a stopper at the top of the chamber. These hooked stoppers were designed for lateral placement of plates about half way between the center and side of the chamber. The height of plates in the chamber was determined by the

0021-8561/85/1433-0891$01.50/0 

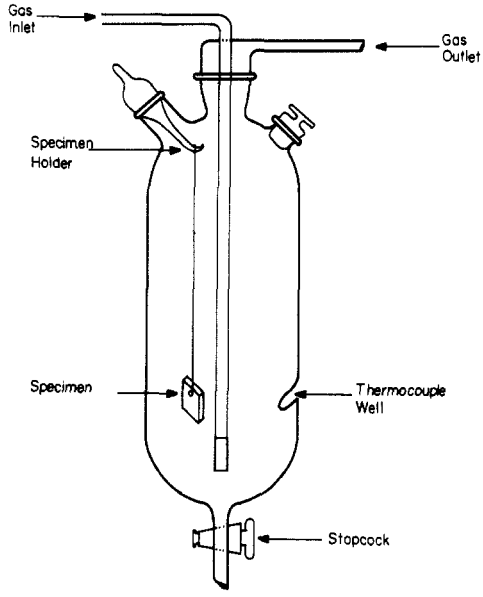


**Figure 1.** Corrosion rate/corrodent chemistry apparatus for the simultaneous measurement of the iron corrosion rate and ascorbate oxidation rate.

choice of thread length. The length chosen in these experiments put the plates at the level of the chamber's thermocouple, about 5 cm from the bottom of the chamber.

Parallel gas distribution was accomplished via an eight-stopcock manifold made of glass. Oxygen gas (99.5% minimum purity, purchased from Liquid Carbonic, Chicago, IL) flowed from the gas tank through the manifold into flowmeters, each connected in series to a corrosion cell with rubber tubing. Gas was dispersed into the cells's solutions through fritted glass on glass tubing that was suspended within 1 cm of the bottom of the cell. Gas made intimate contact with the solution just above the cell's bottom opening, and bubbles of gas rose throughout the entire solution, mixing the contents as well as ensuring intimate gas–liquid contact. Flow meters with aluminum valves (Matheson Co.) monitored gas flow rates in the range of 2–60 mL/min.

The bottom stopcock allowed volumes of solution to be drawn off periodically during the course of an experiment without interrupting the gas flow or disturbing the metal plate(s) inside the cell.

**Kinetic Studies of Ascorbic Acid Oxidation.** Ascorbic acid solutions were prepared by using 99.9% ascorbic acid (Baker analyzed, mp 191 °C) and deionized water. The extent of ascorbic acid oxidation in the chamber solution was determined by withdrawing 5 mL of the solution from the corrosion cell via the stopcock periodically during an experiment, quenching with 8% acetic acid, and titrating with 2,6-dichlorophenolindophenol dye (Sigma Chemicals) to determine reduced ascorbic acid (Freed, 1966). Dye solutions were renewed at least once per week. The use of 8% acetic acid minimized reductive interference of ferrous iron with the dye (Gawron and Berg, 1944). Preliminary work showed ascorbic acid determinations to be reproducible within 4% in 32 titrations. Ascorbic acid oxidation tests were in the 5–6 h range.

The first-order rate constant for each test was calculated by the slope determination of the plot

$$\ln \frac{a}{a-x} \text{ vs. time } (t) \qquad (1)$$

where $a$ = the initial concentration of ascorbic acid at time = 0 in millimoles per liter and $x$ is the ascorbic acid oxidized by time = $t$ hours. Units of the first-order rate constant ($k_1$) are $h^{-1}$. Correlation with first-order kinetic model was very high ($r \geq 0.94$) in all cases but one (where $r = 0.84$) regardless of test length. However, preliminary work showed $k_1$ was smaller when calculated with data from the first 5–6 h of a test than when calculated with all the 10-, 20-, or 40-h data for the same test. Thus, test length was established as a contributor to the variability in calculated first-order rate constants. The half-life ($t_{1/2}$) of ascorbic acid for each test run was calculated as $\ln 2/k_1$. Units of $t_{1/2}$ are in hours.

**Table I. Gravimetric Iron Loss Compared with Total Iron Uptake in Ascorbic Acid Solution**

| gravimetric iron loss, mg | total iron uptake, mg[a] | difference, % |
|---|---|---|
| 5.4 | 5.26 | −3 |
| 5.1 | 4.95 | −3 |
| 6.4 | 6.3 | −2 |
| 10.1 | 10.2 | +1 |
| 4.1 | 3.65 | −12 |
| 10.5 | 10.1 | −4 |

[a] ([Fe] in mg/mL)(volume in mL) = total iron uptake in mg.

**Corrosion Rates.** Corrosion rates were determined gravimetrically by using a Mettler balance capable of distinguishing a weight difference of 0.1 mg. Each plate weight used in gravimetric weight loss calculations represented two consecutive weighings that agreed within 0.1 mg with the balance zeroed before and after each weighing. Preexperimental weighing was performed after an acetone rinse of a prepared plate with air-drying on absorbent paper. Postexperimental weighings were made after a hydrogen bubble treatment in which plates were suspended 5 min in hot concentrated NaOH containing zinc dust (Champion, 1952) and then rinsed in water and then acetone before being air-dried on absorbent paper. Preliminary experiments showed that cleaning and drying procedures had no effect on plate weight, and any 0.2-mg difference between the pre- and postexperimental weights of a plate was treated as a significant gravimetric change brought about by the experimental procedure. Surface areas of plates were calculated from dimensions measured after each experiment with calipers accurate to 0.001 in. Corrosion rate was expressed as mg $cm^{-2}$ $h^{-1}$, one of which is equal to $4.2 \times 10^{-4}$ mdd (mg $cm^{-2}$ $day^{-1}$). Gravimetric corrosion rates were reproducible within a range where the coefficient of variation equaled 29–34%.

Gravimetric changes were corroborated by analyses of solutions for iron concentration using 2,2′-bypyridine method described below. The comparisons agreed well (Table I).

**Iron Samples.** Metal plates were prepared at the Molecular Materials Research Division at Lawrence Berkeley Laboratory. Electrolytic iron of 99.8% purity was heated in an Argon induction furnace to 1775 K, held at this temperature for 15 min, and then poured into molds to make ingots with a cross section of approximately 1 $cm^2$. Plates were cut in square slices (1.5 mm thick) with an abrasive silicon carbide wheel. Cut plates were made smooth with the use of a belt sander and drilled through the face with a 2-mm drill. Before each experiment, iron plates to be tested were polished with finer and finer gradations of emery paper ($Al_2O_3$) from 0 to 0000 grade to assure uniform surface conditions. Kerosene or acetone was the lubricant during polishing. Plates were rinsed between each grade of emery paper. After polishing, plates were rinsed in acetone, dried with forced air, and stored in a desiccator until weighing. Six iron plates were used, repolished, and reused in all experiments. At the com-

**Table II. Gravimetric Corrosion Rates of Iron Plates in 1.14 mM Ascorbic Acid Solution for 6.0 h**

| gravimetric wt loss, mg | corrosion rate mg/h | mg $cm^{-2}$ $h^{-1}$ | mdd[a] |
|---|---|---|---|
| 5.5 | 0.92 | 0.21 | 504 |
| 3.8 | 0.63 | 0.14 | 336 |
| 2.5 | 0.42 | 0.097 | 233 |
| 3.6 | 0.60 | 0.13 | 312 |
| 3.4 | 0.57 | 0.14 | 336 |
| 6.1 | 1.02 | 0.26 | 624 |
| 4.9 | 0.82 | 0.19 | 456 |
| 3.1 | 0.52 | 0.12 | 288 |
| 4.1 | 0.68 | 0.14 | 336 |
| 4.3 | 0.72 | 0.15 | 360 |
| 3.25 | 0.54 | 0.12 | 288 |
| 3.0 | 0.50 | 0.13 | 312 |
| $\bar{X}$ | 0.66 | 0.15 | 365 |
| SD | 0.18 | 0.046 | 110 |
| CV, % | 27 | 31 | 30 |

[a] mdd = mg $dm^{-2}$ $day^{-1}$

pletion of experimental work these plates were shown to be 99.8% iron and less than 0.01% copper by analysis conducted at Anamet Laboratories in Berkeley, CA.

In six experiments a fine electrolytic iron powder (99.9% purity) purchased from Materials Research Corp., Orangeburg, NY (lot no. 31546) was used as the corroding material. Iron powder was weighed on the Mettler balance and mixed with solutions in a volumetric flask before being poured into the corrosion cell. The iron powder did not dissolve completely or instantaneously, and the gas flow system kept these fine iron particles suspended in the solution. The solutions in these cases should be viewed as containing increasing amounts of dissolved iron and decreasing amounts of fine iron particles in suspension. Measurement of quantitative corrosion rates for these systems was not attempted. Iron analyses were performed on these solutions to determine the amount of total or dissolved iron at the end of an experiment. Analysis of the iron powder at completion of experimental work showed it to be 99.5% iron containing 0.03% copper by weight (Anamet Laboratories).

**Iron Analyses.** Iron analyses were made using 2,2′-bypyridine (Schaefer, 1969).

**Statistical Analysis.** Rate constant ($k_1$) data were grouped according to iron treatment (–Fe, +Fe plate, +Fe powder), and one-way analysis of variance was performed on ln $k_1$ data with an $\alpha$ level = 0.05, using the Statistical Package for the Social Sciences program on an IBM 4341 computer. Correlation coefficients ($r$), $k_1$ values, half-lives ($t_{1/2}$), means ($\bar{X}$), standard deviations (SD), and coefficients of variation (CV) were calculated on a hand statistical calculator that was checked periodically against another hand calculator of a different make.

## RESULTS

**Corrosion of Iron in Ascorbic Acid.** *Corrosion Rate of Iron in Ascorbic Acid.* Gravimetric corrosion rates of iron plates in 1.14 mM ascorbic acid solution appear in Table II. The mean of 12 tests was 0.15 mg/$cm^{-2}$ $h^{-1}$ (365 mdd) with a CV equal to 31%. Sources of error included minor differences in ascorbic acid concentration, temperature, and surface preparation from test to test, plus error in plate dimension and weight measurements.

*Effect of Ascorbic Acid Concentration.* Iron corrosion rates in deionized water and six concentrations of ascorbic acid are shown in Figure 2. Each concentration was tested with only one plate except for 0.57 mM ascorbate in which duplicates were tested. The trend clearly showed an enhancement of the corrosion rate of iron with increasing concentrations of ascorbic acid. The correlation coefficient was significantly different from zero for the data ($r$ = 0.982,

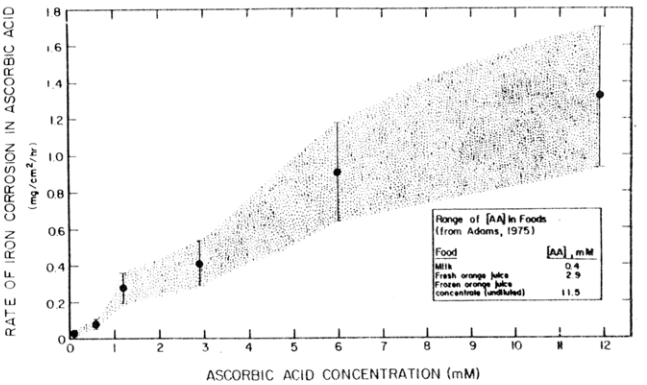


**Figure 2.** Effect of ascorbic acid concentration on the iron corrosion rate measured gravimetrically. Points represent the corrosion rate of one 5-h test with ±30% added as presumed variability.

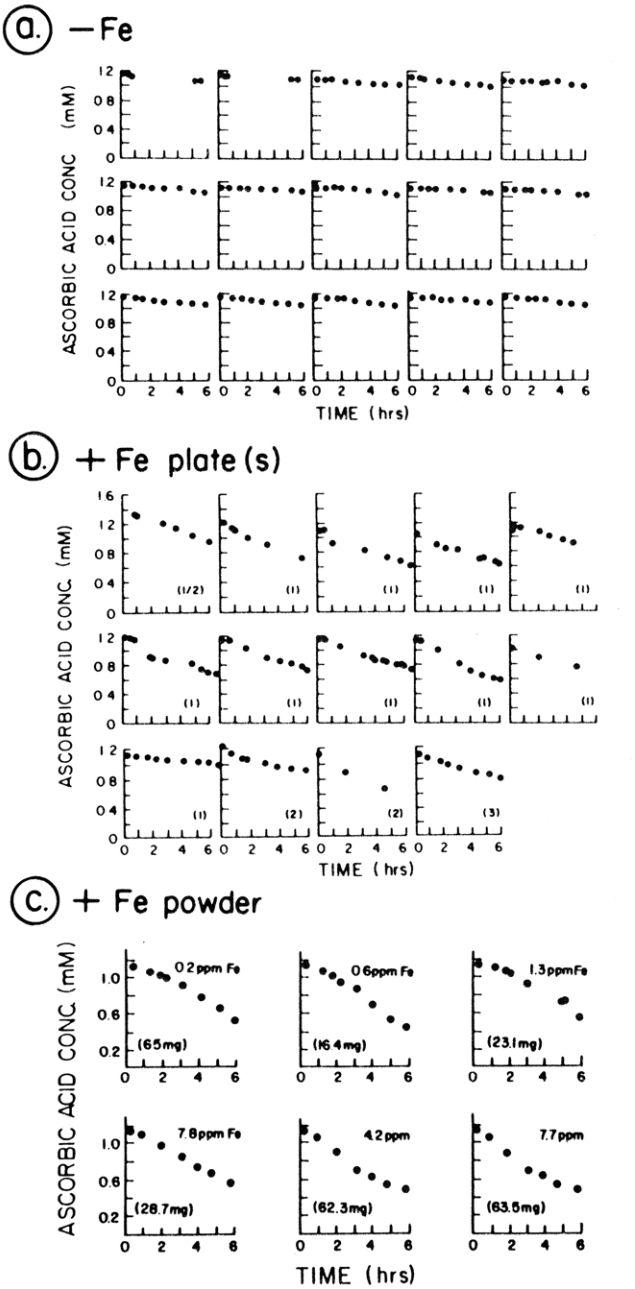


**Figure 3.** Degradation of oxygenated 1.14 mM ascorbic acid under three types of treatment. (a) No Fe present. (b) Fe plate(s) present. Numbers in ( ) denote quantity of iron plates present in the 1.0 L chambers. Surface area per plate approximately 2 $cm^2$. (c) Fe powder present in amount denoted in ( ). Final dissolved [Fe] appears in upper right hand corners.

**Table III. First-Order Rate Constant ($k_1$) and Half-Life ($t_{1/2}$) for Ascorbic Acid[a] Oxidation in the Presence and Absence of Elemental Iron**

| Fe treatment | $n$ | | length of test, h | $K_1$, $h^{-1}$ | $t_{1/2}$, h | final [Fe], ppm |
|---|---|---|---|---|---|---|
| no Fe present | 15 | $\bar{X}$ | 5.93 | 0.0141 | 52.5 | |
| | | SD | 0.269 | 0.00368 | 13.5 | 0 |
| | | CV, % | 4.5 | 26.1 | 25.7 | |
| +Fe plate(s) | 14 | $\bar{X}$ | 6.08 | 0.0698 | 12.1 | |
| | | SD | 0.898 | 0.0258 | 7.57 | 3.1–10.6 |
| | | CV, % | 14.8 | 37.0 | 63 | |
| +Fe powder | 6 | $\bar{X}$ | 6.02 | 0.139 | 5.15 | |
| | | SD | 0.0753 | 0.0252 | 1.02 | 0.2–7.8 |
| | | CV, % | 1.25 | 18.1 | 19.8 | |

[a] 1.14 mM concentration.

$n$ = 9). The error band shown in Figure 2 assumes a 30% variability with each measurement as a mean. The corrosion of iron in deionized water was essentially zero for these types of tests.

*Effect of Oxygen Flow Rate.* In one experiment four chambers were varied in oxygen flow rate from 2 to 60 mL/min, and corrosion rates of iron plates in 1.14 mM ascorbic acid were determined. Regression of the corrosion rate on the flow rate showed a negative slope and a correlation coefficient that did not differ significantly from zero ($r$ = –0.5, $n$ = 4).

**Catalysis of Ascorbic Acid Oxidation by Iron Corrosion Products.** Results of the kinetic studies for ascorbate oxidation are presented in Table III. Degradation curves appear in Figure 3.

*Ascorbic Acid Oxidation with No Iron Present.* When tested as a first-order rate curve, all but 1 of these 15 tests showed correlation coefficients greater than or equal to 0.94, and 1 was equal to 0.84. The range of $k_1$ for these tests was from 0.0087 to 0.021 $h^{-1}$ with a mean of 0.014 $h^{-1}$.

*Ascorbic Acid Oxidation with One, Two, or Three Iron Plates Present.* Each of the 14 tests showed a correlation coefficient greater than or equal to 0.95 when tested as a first-order kinetic reaction. The range of these first-order rate constants was 0.0192–0.116 $h^{-1}$, the mean was 0.0698 $h^{-1}$, about 5× and significantly different from the mean $k_1$ for identical solutions not exposed to iron. With a CV of 37%, variability about the mean was greater for these data than for the tests without any iron present due to the wider range of test length in these data (4.6–6.9 h) (see Materials and Methods).

Tests with two or three corroding iron plates did not exhibit greater or lesser rates of ascorbic acid oxidation than tests with one plate. Thus, greater amounts of iron corrosion did not cause a higher ascorbic acid oxidation rate. The correlation coefficient for $k_1$ and total corrosion in mg Fe did not differ significantly from zero ($r$ = –0.357, $n$ = 14).

*Ascorbic Acid Oxidation with Iron Powder Present.* All six experiments showed correlation coefficients greater than or equal to 0.97 when compared with the first-order kinetic model. First-order rate constants for these data ranged from 0.101 to 0.167 $h^{-1}$. The mean $k_1$ was 0.139 $h^{-1}$, twice that of identical ascorbic acid solutions facing iron plates and 10 times that of solutions free of added iron. The CV for these data (18.1%) was less than that of the other $k_1$ data sets. These tests were the most uniform in test length and spacing of titrations. Such control in acquiring data for rate calculations decreased the variability in rate constants.

Weights of iron powder used in these six experiments varied from about 6 to 60 mg/L, and dissolved iron as measured colorimetrically ranged from 0.2 to about 8 ppm. The correlation coefficient for $k_1$ and iron concentration ($r$ = 0.106, $n$ = 6) and for $k_1$ and weight of iron powder introduced to the solution ($r$ = 0.4, $n$ = 6) did not differ significantly from zero. Therefore, as with the tests with iron plates, these data do not support the hypothesis that an increase in iron corrosion rate or iron concentration will augment ascorbic acid oxidation.

**Table IV. Iron-Catalyzed First-Order Rate Constant and Half-Life for 1.14 mM Ascorbic Acid[a] Oxidation in the Presence of Oxygen and Ascorbic Acid Oxidation Products**

| % oxidized | length of test, h | $n$ | $r$ | $k_1$, $h^{-1}$ | $t_{1/2}$, h | no. of plates of Fe present |
|---|---|---|---|---|---|---|
| 80 | 0.18 | 3 | 0.9999 | 2.39 | 0.29 | 1 |
| 67 | 0.25 | 4 | 0.954 | 17.08 | 0.041 | 1 |

[a] 1.14 mM concentration.

**Table V. Rate of Ascorbic Acid Solutions' Iron Uptake from Submerged Iron Plate(s)**

| ascorbic acid concn, mM | no. of Fe plates | $n^a$ | $r^b$ | Fe uptake rate, ppm/h |
|---|---|---|---|---|
| 1.20 | 1 | 16 | 0.98 | 0.679 |
| 1.14 | 1 | 4 | 0.998 | 0.586 |
| 1.15 | 2 | 7 | 0.987 | 1.36 |
| 1.14 | 3 | 4 | 0.992 | 1.62 |
| 2.86 | 1 | 3 | 0.999 | 2.00 |
| 1.1–1.2 | 1 | 20 | 0.983 | 0.620 |

[a] $n$: number of [Fe] determinations. [b] $r$: correlation coefficient between time and [Fe].

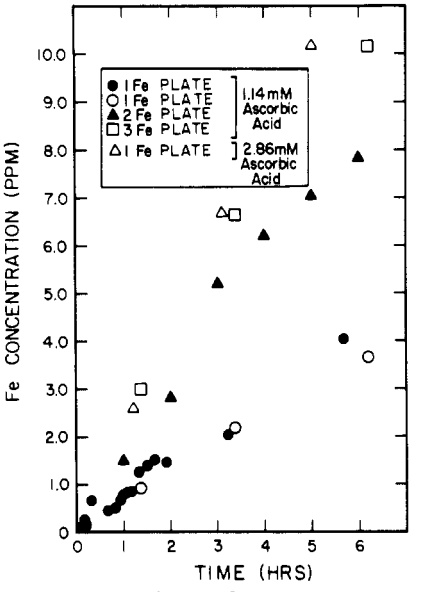


**Figure 4.** Rate of ascorbic acid solutions' iron uptake from submerged iron plate(s).

Data are presented in Table IV from tests where iron plates were immersed in solutions of ascorbic acid that were more than 50% oxidized. The presence of ascorbic acid oxidation products greatly enhanced the catalytic effect of the iron plates. Two very short tests showed that the complete, rapid oxidation of the ascorbic acid did not occur immediately: 3 min after immersion, the noncatalyzed oxidation rate had not significantly changed. Ten minutes after plate immersion both solutions had dropped in reduced ascorbic acid by well over 50%, and 15 min after immersion reduced ascorbic acid had dropped to zero in both tests.

## DISCUSSION

**Corrosion of Iron in Ascorbic Acid.** Iron concentrations in parts per million (ppm) vs. time for five corrosion experiments in ascorbic acid are plotted in Figure 4. Iron uptake rates were calculated as the slope of these curves, and the results are tabulated in Table V. The

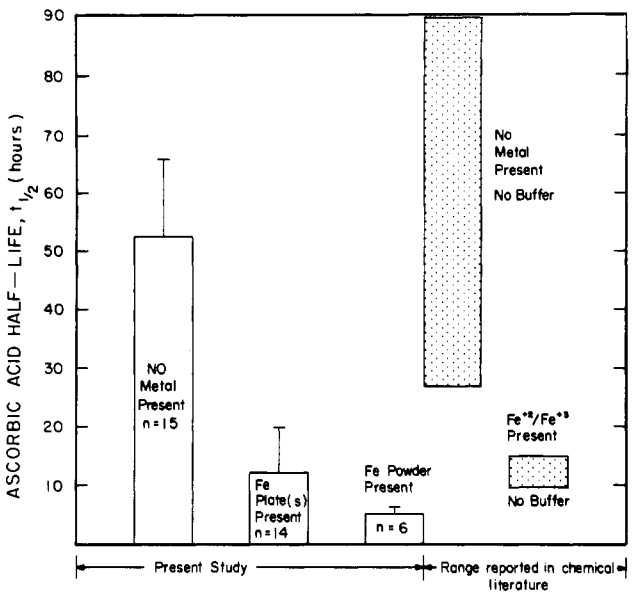


**Figure 5.** Half-life comparison of ascorbic acid under conditions of this study and as reported in the literature. T denotes standard deviation.

corrosion-enhancing effects of both ascorbic acid concentration and total surface area of exposed plates are clearly evident in these data. No tests proved to be absolutely linear; all iron uptake rates dropped off slightly with time. Thus, the corrosion rate was very gradually declining in these short tests in ascorbic acid; however, the trend is generally linear with no abrupt changes in the rate of change of iron concentration.

The surface area of each iron plate was approximately 2 $cm^2$, and the total volume of solution in the chambers was 1 L. The ratio of iron surface area to volume of solution for these tests was thus 2–6 $cm^2/L$. Iron uptake rates for these rather dilute solutions of ascorbic acid ranged from 0.5 to 2 ppm/h at room temperature. The surface area to volume ratio in an iron skillet is 200–500 $cm^2$ of iron/L of solution. Clearly, substantial amounts of iron could be expected to enter a food high in ascorbic acid prepared under such conditions.

**Ascorbic Acid Oxidation by Iron Corrosion Products.** Mean half-lives ($t_{1/2}$) ± SD for the three treatments of ascorbic acid are presented in Figure 5 with $t_{1/2}$ values calculated from data of other investigators. In the present study $t_{1/2}$ for noncatalyzed ascorbic acid oxidation ranged from 33 to 79.5 h. Calculated literature values for ascorbic acid $t_{1/2}$ in nonbuffered, noncatalyzed acid solution range from 27 to 89 h in tests of 2 h to several days' length (Kellie and Zilva, 1935; Giral, 1947; Sattar et al., 1977). The variability of ascorbic acid oxidation $k_1$ and $t_{1/2}$ values seems high but is explained by the error in reproducibility for ascorbic acid determinations, which, in this and most other cases, was by titration with indophenol dye. Consider a 6-h ascorbic acid oxidation run starting with a solution of 0.90 mg of ascorbic acid/5.0 mL at 6.0 h. With only a 3.0% error in the method of ascorbic acid determination, calculated $k_1$ values would range from 0.00702 to 0.0281 $h^{-1}$. The low level of oxidation of ascorbic acid in acidic media and an error of only 3% in ascorbate determinations makes the large range of $k_1$ and $t_{1/2}$ values for this measurement inevitable.

The half-life for ascorbic acid solutions in the presence of elemental iron as plates ranged from 6.0 to 16.6 h for 13 tests with 1 test showing a $t_{1/2}$ = 36.1 h. The mean ± SD for these data are shown in Figure 5 with the range of $t_{1/2}$ values calculated with data from the literature for ferric/ferrous ion catalyzed ascorbic acid oxidation in nonbuffered solutions. These literature $t_{1/2}$ values range from 10 to 15 h for iron concentrations of 0.25 to 10 ppm as various iron salts in tests ranging from 2- to 20-h duration (Kellie and Zilva, 1935; Mack and Kertesz, 1936; Sattar et al., 1977). These few values compare well with those obtained in the present study with elemental iron.

Ascorbic acid $t_{1/2}$ values from this study when iron powder was present were shorter than with iron plates and the values for iron-catalyzed ascorbic acid degradation in the literature. This could be due to differences in surface conditions when powders are used in place of solid plate of iron. However, the slight copper impurity found in the iron powder used in this study could be the cause of this discrepancy even though the maximum copper concentration possible in these solutions was only 3 parts per billion (ppb), a full order of magnitude less than the 0.05-ppm copper contamination level deemed safe and appropriate for noncatalyzed ascorbic acid studies (Barron et al., 1936; Timerlake, 1960). Joslyn and Miller (1949) reported very similar $t_{1/2}$ values when 0.07-ppm levels of both cupric and ferric ion were present in ascorbic acid solutions of pH similar to the present study. However, their levels of copper were 23 times that of the theoretical maximum of the present study so the larger surface area and different physical properties presented by iron powders cannot be ruled out as a cause of this statistically significant result.

In this study, pure ascorbic acid solutions showed the same oxidation rate regardless of the iron concentration due to corrosion. This is in contrast to the work of Taqui-Khan and Martell (1967), who found increasing $k_1$ values with increasing iron concentration in acetate buffer systems. However, this result corroborates the work of Joslyn and Miller (1949), who found no differences in ascorbic acid $k_1$ when iron concentration was doubled in phosphate buffer, and Sattar et al. (1977), who found no increase in ascorbic acid oxidation with increasing iron concentrations from 2 to 10 ppm (no buffers present). These results imply that a minimal amount of iron corrosion into ascorbic acid solution will cause the same rate of ascorbate degradation as larger amounts of iron contamination. Nutritionally, then, small iron corrosion rates in foods will have the same detrimental effect on vitamin C without the advantage of raising the iron content substantially. Such may be the case with stainless steels that contain approximately 74% iron and tend toward localized types of corrosion such as pitting and crevice corrosion rather than the uniform type of corrosion exhibited by iron, cast irons, and steels (Sedriks, 1979; Fontana and Green, 1978).

Addition of metallic iron to foods inadvertently or in the form of iron enrichment powders represents cases of a food being faced with corroding iron. The processing or preparation of foods in iron-containing equipment can be expected to present foods with large amounts of corroding iron in the case of steels and cast irons and small, localized amounts of corroding iron in the case of stainless steels.

It has been held that such addition of iron to foods via corrosion reactions is beneficial nutritionally if it is not in excess as in the case of the male Bantu (Walker and Arvidsson, 1953). The simultaneous oxidation of ascorbic acid to dehydroascorbic acid necessitates a reassessment of this presumption. Nutritionally, the production of dehydroascorbic acid does not mean the full destruction of vitamin C activity, but many studies in food systems show rapid degradation of nutritionally active dehydroascorbic acid once it is produced (Davidek et al., 1974; Domah et al., 1974; Marchesini et al., 1975; Smoot and Nagy, 1980).

This study has clearly shown ascorbic acid to be one component of food responsible for iron "leaching" from pots, pans, and processing equipment. The addition of ascorbic acid to foods during processing can be expected to affect the food's corrosive properties. Also, the addition of reduced iron either intentionally or from inadvertent corrosion processes can be expected to substantially accelerate the rate of vitamin C degradation in some foods.

ACKNOWLEDGMENT

We thank Dr. David P. Whittle and Dr. Haroun Hindam of MMRD at Lawrence Berkeley Laboratory for generous support for this project and iron plate preparation.

**Registry No.** Ascorbic acid, 50-81-7; iron, 7439-89-6.

LITERATURE CITED

Barron, E. S. G.; De Meio, R. H.; Klemperer, F. *J. Biol. Chem.* **1936**, *112*, 625.
Burroughs, A. L.; Chan, J. J. *J. Am. Diet. Assoc.* **1972**, *60*, 123.
Champion, F. A. "Corrosion Testing Procedures"; Chapman and Hall: London, 1952.
Chatt, E. M. *World Rev. Nutr. Diet.* **1964**, *4*, 141.
Cunningham, H. M.; O'Brien, R. *J. Food Sci.* **1972**, *37*, 572.
Davidek, J.; Velisek, J.; Janicek, G. *Lebensm.-Wiss. Technol.* **1974**, *7*, 285.
Derman, D. P.; Bothwell, T. H.; Torrance, J. D.; Bezwoda, W. R.; MacPhain, A. P.; Kew, M. C.; Sayers, M. H.; Disler, P. B.; Charlton, R. W. *Br. J. Nutr.* **1980**, *43*, 271.
Devadas, R. P.; Chandrasekhar, U.; Kumari, K. S. *Indian J. Nutr. Diet.* **1973**, *10*, 223.
Domah, A. A. M. B.; Davidek, J.; Velisek, J. *Z. Lebensm.-Unters. -Forsch.* **1974**, *154*, 270.
Fontana, M. G.; Green, M. D. "Corrosion Engineering", 2nd ed.; McGraw-Hill: New York, 1978.
Freed, M. "Methods of Vitamin Assay", 3rd ed.; Interscience: New York, 1966.
Gawron, O.; Berg, R. *Ind. Eng. Chem., Anal. Ed.* **1944**, *16*, 757.
Giral, F. *J. Am. Pharm. Assoc.* **1947**, *36*, 82.
Hegenauer, J.; Saltman, P.; Ludwig, D. *J. Dairy Sci.* **1979**, *62*, 1037.
Joslyn, M. A.; Miller, J. *Food Res.* **1949**, *14*, 325.
Kellie, A. E.; Zilva, S. S. *Biochem. J.* **1935**, *29*, 1028.
Mack, G. L.; Kertesz, Z. I. *Food Res.* **1936**, *1*, 377.
MacKay, H. M. M.; Dobbs, R. H.; Bingham, K. *Arch. Dis. Child.* **1945**, *20*, 56.
Marchesini, A.; Majorino, G.; Montuori, R.; Cagna, D. *J. Food Sci.* **1975**, *40*, 665.
Massini, R. *Ind. Conserve* **1975**, *50*, 3.
Moore, C. V. *Ser. Haematol.* **1965**, *6*, 1.
Muneta, P. *Mater. Perform.* **1975**, *14*, 30.
Rosanoff, A.; Kennedy, B. M. *J. Food Sci.* **1982**, *47*, 609.
Sattar, A.; DeMan, J. M.; Alexander, J. C. *Can. Inst. Food Sci. Technol. J.* **1977**, *10*, 65.
Schaefer, W. C. "Approved Methods of the American Association of Cereal Chemists"; American Association of Cereal Chemists: St. Paul, MN, 1969.
Sedricks, A. J. "Corrosion of Stainless Steels"; Wiley: New York, 1979.
Selby, J. W. *Sci. Tech. Surv.—Br. Food Manuf. Ind. Res. Assoc.* **1954**, *24*, 2.
Smoot, J. M.; Nagy, S. *J. Agric. Food Chem.* **1980**, *28*, 417.
Taqui-Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1967**, *89*, 4176.
Timberlake, F. C. *J. Sci. Food Agric.* **1960**, *11*, 258.
Walker, A. R. P.; Arvidsson, U. B. *Trans. R. Soc. Trop. Med. Hyg.* **1953**, *47*, 536.

Received for review September 19, 1983. Accepted September 5, 1984. Presented at the 185th National Meeting of the American Chemical Society, Seattle, WA, March 1983, AGFD 13. Funds for this project were provided by the Chancellor's Patent Fund, University of California, Berkeley.

# Detection, Isolation, and Identification of Impurities in Technical Thiofanox

Russell Buchman,* Richard A. Komoroski,[1] Kenneth M. Kauppila, James J. Mannion, and Lane Gehrlein[2]

The detection, isolation, and identification of the impurities in the technical grade of the insecticide thiofanox are described. A $^{13}C$ NMR method was employed to detect impurities at about the 0.1% level or greater. The $^{13}C$ spectrum of very high signal-to-noise ratio of an impurity concentrate was used to guide subsequent separation and identification work. The sensitivity and reliability of this approach are discussed. Preparative and semipreparative high performance liquid chromatography was employed to isolate 39 nonvolatile components. These were identified on the basis of spectral data and by comparisons with authentic samples which were synthesized when necessary. Some stereochemical assignments are made on the basis of NMR chemical shifts. An additional 30 volatile components were isolated and identified by vacuum distillation and gas chromatography/mass spectrometry.

## INTRODUCTION

The detection, identification, and quantification of impurities in technical pesticides are problems of scientific, economic, and social importance. Government regulations will continue to make it increasingly difficult for industry to register new pesticide products. The need to characterize technical pesticides in greater detail, and the increasing complexity of the chemical structures involved, necessitates the development of more sophisticated analytical methods than presently exist (Donaldson and Garrison, 1979; Fed. Regis., 1978; Libby and Freeberg, 1978).

Technical pesticides will generally be complex mixtures of components because of process variables, side reactions, and impurities in starting materials. It is reasonable to expect that many of the impurities will be similar in chemical structure to the major component. In some cases, the existence of geometrical isomers or diastereomers can further complicate characterization efforts.

SDS Biotech Corporation, Painesville, Ohio 44077.
[1]Current address: BF Goodrich Research Center, Brecksville, OH 44141.
[2]Current address: Lederle Laboratories, Pearl River, NY 10965.

0021-8561/85/1433-0896$01.50/0 