Kirk-Othmer Encyclopedia of Chemical Technology.

FORMIC ACID

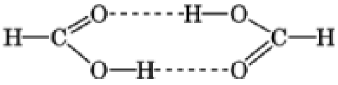
Formic acid [64-18-6] (methanoic acid) is the first member of the homologous series of alkyl carboxylic acids. It occurs naturally in the defensive secretions of a number of insects, particularly of ants. Although the acid nature of the vapors above ants' nests had been known since at least 1488, the pure acid was not isolated until 1671, when the British chemist John Ray described the isolation of the pure acid by distillation of ants (1). This remained the main preparative method for more than a century until a convenient laboratory method was discovered by Gay-Lussac (2). The preparation of formates using carbon monoxide was described by Berthelot in 1856.

Formic acid was a product of modest industrial importance until the 1960s when it became available as a by-product of the production of acetic acid by liquid-phase oxidation of hydrocarbons. Since then, first-intent processes have appeared, and world capacity has climbed to around 330,000 t/yr, making this a medium-volume commodity chemical. Formic acid has a variety of industrial uses, including silage preservation, textile finishing, and as a chemical intermediate.

1. Physical Properties

Formic acid is a colorless, highly corrosive liquid with an intense and pungent smell. Its basic physical properties are given in Table 1. Formic acid is totally miscible with water, acetone, ether, ethyl acetate, methanol, and ethanol. It dissolves to the extent of about 10% in benzene, toluene, and xylenes and to a lesser extent in aliphatic hydrocarbons. Formic acid is unusual in forming a high boiling azeotrope (bp = 107°C at normal pressure) with water, containing 77.5% by weight of the acid. Azeotropic mixtures are also formed with many other substances (12). Formic acid and water form a eutectic mixture which freezes at $-48.5°C$ and contains 70% by weight of formic acid.

In the vapor phase formic acid forms a hydrogen-bonded dimer:

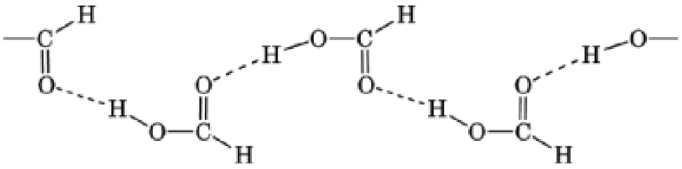


At room temperature and atmospheric pressure, 95% of the vapor consists of dimers (13). The properties of the vapor deviate considerably from ideal gas behavior because of the dimerization. In the solid state, formic acid forms infinite chains consisting of monomers linked by hydrogen bonds (14):

Table 1. Physical Properties of Pure Formic Acid

Property	Value	Reference
molecular weight	46.026	
melting point, °C	8.4	3
boiling point, °C	100.7	4
density, g/cm^3 at 20°C	1.220	5
refractive index n_D^{20}	1.3714	5
surface tension at 20°C, mN/m(= dyn/cm)	37.67	6
viscosity at 20°C, mPa·s(= cP)	1.784	7
specific conductance, Ω/m	6.08×10^{-3}	8
dielectric constant at 20°C	57.9	9
latent heat of vaporizationat boiling point, kJ/kg^a	483	10
free energy of formation, ΔG_f^0(g), kJ/mol^a	−351	11
enthalpy of formation, ΔH_f^0(g), kJ/mol^a	−377	11

[a] To convert kJ to kcal, divide by 4.184.

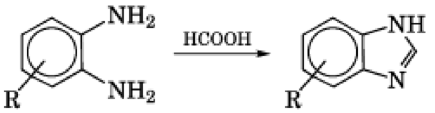


The chain structure persists in liquid formic acid, but in solution in hydrocarbons the dimeric form predominates (15).

2. Chemical Properties

Formic acid exhibits many of the typical chemical properties of the aliphatic carboxylic acids, eg, esterification and amidation, but, as is common for the first member of an homologous series, there are distinctive differences in properties between formic acid and its higher homologues. The smaller inductive effect of hydrogen in comparison to an alkyl group leads, for example, to formic acid ($pK_a = 3.74$) being a considerably stronger acid than acetic acid ($pK_a = 4.77$) (16) and in fact the strongest of the simple, unsubstituted carboxylic acids. The formyl hydrogen can also be looked on as conferring some aldehydic character, and formic acid, for example, reduces aqueous silver nitrate to produce metallic silver.

Formic acid forms esters with primary, secondary, and tertiary alcohols. The high acidity of formic acid makes use of the usual mineral acid catalysts unnecessary in simple esterifications (17). Formic acid reacts with most amines to form formylamino compounds. With certain diamines imidazole formation occurs, a reaction that has synthetic utility (18):

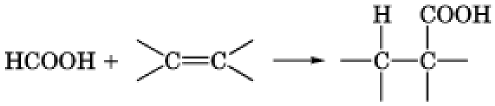


Formic acid can decompose either by dehydration, $HCOOH \longrightarrow H_2O + CO$ ($\Delta G^0 = -30.1$ kJ/mol; $\Delta H^0 = 10.5$ kJ/mol) or by dehydrogenation, $HCOOH \longrightarrow H_2 + CO_2$ ($\Delta G^0 = -58.6$ kJ/mol; $\Delta H^0 = -31.0$ kJ/mol). The kinetics of these reactions have been extensively studied (19). In the gas phase metallic catalysts favor dehydrogenation, whereas oxide catalysts favor dehydration. Dehydration is the predominant mode of decomposition in the liquid phase, and is catalyzed by strong acids. The mechanism is believed to be as follows (19):

$$HCOOH + H^+ \longrightarrow HCOOH_2^+ \longrightarrow HCO^+ + H_2O$$

$$HCO^+ \longrightarrow H^+ + CO$$

The formyl cation, HCO^+, is also likely to be an intermediate in the modification of the Koch reaction whereby formic acid reacts with olefins to give carboxylic acids (20):



This reaction occurs readily in the presence of sulfuric or hydrofluoric acid. In the absence of such strong acids, formic acid reacts readily with olefins to give formate esters (21).

The anhydride of formic acid has not been isolated, but mixed anhydrides are known, and, with acetic acid, the latter have utility as formylating agents (22). The only known formyl halide is the fluoride, which has a boiling point of $-29°C$.

3. Manufacture

Formic acid is currently produced industrially by three main processes: (*1*) acidolysis of formate salts, which are in turn by-products of other processes; (*2*) as a coproduct with acetic acid in the liquid-phase oxidation of hydrocarbons; or (*3*) carbonylation of methanol to methyl formate, followed either by direct hydrolysis of the ester or by the intermediacy of formamide.

The reaction of formate salts with mineral acids such as sulfuric acid is the oldest industrial process for the production of formic acid, and it still has importance in the 1990s. Sodium formate [141-53-7] and calcium formate [544-17-2] are available industrially from the production of pentaerythritol and other polyhydric alcohols and of disodium dithionite (23). The acidolysis is technically straightforward, but the unavoidable production of sodium sulfate is a clear disadvantage of this route.

Liquid-phase oxidation of lower hydrocarbons has for many years been an important route to acetic acid [64-19-7]. In the United States, butane has been the preferred feedstock, whereas in Europe naphtha has been used. Formic acid is a coproduct of such processes. Between 0.05 and 0.25 tons of formic acid are produced for every ton of acetic acid. The reaction product is a highly complex mixture, and a number of distillation steps are required to isolate the products and to recycle the intermediates. The purification of the formic acid requires the use of azeotroping agents (24). Since the early 1980s hydrocarbon oxidation routes to acetic acid have declined somewhat in importance owing to the development of the rhodium-catalyzed route from CO and methanol (see Acetic acid).

The carbonylation of methanol [67-56-1] to methyl formate in the presence of basic catalysts has been practiced industrially for many years. In older processes for formic acid utilizing this reaction, the methyl formate [107-31-3] reacts with ammonia to give formamide [75-12-7], which is hydrolyzed to formic acid in the presence of sulfuric acid:

$$2\ CO + 2\ CH_3OH \longrightarrow 2\ HCOOCH_3 \xrightarrow{2\ NH_3} 2\ HCONH_2 + 2\ CH_3OH$$

$$2\ HCONH_2 + H_2SO_4 + 2\ H_2O \longrightarrow 2\ HCOOH + (NH_4)_2SO_4$$

Coproduction of ammonium sulfate is a disadvantage of the formamide route, and it has largely been supplanted by processes based on the direct hydrolysis of methyl formate. If the methanol is recycled to the carbonylation step the stoichiometry corresponds to the production of formic acid by hydration of carbon monoxide, a reaction which is too thermodynamically unfavorable to be carried out directly on an industrial scale.

$$CO + CH_3OH \longrightarrow HCOOCH_3$$

$$HCOOCH_3 + H_2O \longrightarrow HCOOH + CH_3OH$$

$$CO + H_2O \longrightarrow HCOOH$$

A number of variants of this process have been patented (25). The conditions for the carbonylation step are broadly similar in each, but they differ in their approach to the hydrolysis stage.

The carbonylation of methanol to give formic acid is carried out in the liquid phase with the aid of a basic catalyst such as sodium methoxide. It is important to minimize the presence of water and carbon dioxide in the starting materials, as these cause deactivation of the catalyst. The reaction is an equilibrium, and elevated pressures are necessary to give good conversions. Typical reaction conditions appear to be 80°C, 4.5 MPa (44 atm) pressure and 2.5% w/w of catalyst. Under these conditions the methanol conversion is around 30% (25).

The hydrolysis of methyl formate is technologically demanding for a number of reasons. The hydrolysis equilibrium is relatively unfavorable (26), but is dependent on the water concentration in a way that favors the use of high stoichiometric excesses of water, with consequent problems of finding an energy-efficient method of removing the excess water. Furthermore, methyl formate is highly volatile ($bp = 32°C$) and formic acid is a sufficiently strong acid to catalyze the reesterification. It is therefore difficult to remove unreacted methyl formate without a significant amount of reesterification. In the Kemira-Leonard process (27) these problems are overcome by use of two hydrolysis reactors in series, followed by flash distillation to rapidly remove unconverted ester and distillation in a column of low residence time. The process operated by BASF (25) uses hydrolysis in the presence of a large excess of water followed by liquid–liquid extraction of formic acid with a nitrogen base and subsequent distillation. The process operated in the Ukraine (28) uses a fixed bed of cationic ion-exchange resin as hydrolysis catalyst. Other approaches to the hydrolysis problem have also been patented (29, 30).

Other potential processes for production of formic acid that have been patented but not yet commercialized include liquid-phase oxidation (31) of methanol to methyl formate, and hydrogenation of carbon dioxide (32). The catalytic dehydrogenation of methanol to methyl formate (33) has not yet been adapted for formic acid production.

4. Shipping and Storage

Formic acid is commonly shipped in road or rail tankers or drums. For storage of the 85% acid at lower temperatures, containers of stainless steel (ASTM grades 304, 316, or 321), high density polyethylene, polypropylene, or rubber-lined carbon steels can be used (34). For higher concentrations, Austenitic stainless steels (ASTM 316) are recommended.

The DOT hazard classification of formic acid is “corrosive material.” A DOT white label is mandatory for transportation. The EC classification is “corrosive.”

Attention must be paid to the fact that formic acid, particularly at higher concentrations and temperatures, can, on storage, slowly decompose to liberate carbon monoxide. This can lead to safety hazards from the ensuing buildup in pressure or from the toxicity of carbon monoxide. It has been estimated that, in the absence of leakage, a full 2.5-L bottle of formic acid could develop a pressure of over 700 kPa (7 atm) over a period of one year at 25°C (35).

Table 2. Specifications for Commercial Formic Acid

Property	Value
appearance	clear, free from matter in suspension
color	20 Hazen maximum
assay	98 or 85% mass minimum
nonvolatile matter	0.005% mass maximum
chloride as Cl^-	3 ppm maximum
sulfate as SO_4^{2-}	5 ppm maximum
iron as Fe	2 ppm maximum

5. Economic Aspects

World installed capacity for formic acid is around 330,000 t/yr. Around 60% of the production is based on methyl formate. Of the remainder, about 60% comes from liquid-phase oxidation and 40% from formate salt-based processes. The largest single producer is BASF, which operates a 100,000 t/yr plant at Ludwigshafen in Germany. The only significant U.S. producer of formic acid is Hoechst-Celanese, which operates a butane oxidation process.

The principal use worldwide for formic acid is as a silage additive, an application that is not well developed in the United States; the U.S. market for formic acid is therefore relatively small (ca 30,000 t/yr) by world standards. Typical U.S. prices for formic acid (mid-1992) were around $0.90/kg.

6. Specifications and Analytical Methods

Formic acid is manufactured in concentrations of 85, 90, 95, 98, and $>99\%$, the diluent being water. A typical product sales specification is given in Table 2 (36).

The concentration of aqueous solutions of the acid can be determined by titration with sodium hydroxide, and the concentration of formate ion by oxidation with permanganate and back titration. Volatile impurities can be estimated by gas–liquid chromatography. Standard analytical methods are detailed in References 37 and 38.

7. Health and Safety Factors

The main hazard in normal handling of formic acid is likely to arise from its corrosive effect on the skin and mucous membranes. Suitable protective equipment should be worn when handling the acid, and rubber or PVC gloves, rubber boots, and goggles are needed during bulk handling operations. In the event of contact with the skin, the affected area should be washed thoroughly with water, and medical attention should be obtained if redness and blistering occur and persist. Medical attention should be sought in all cases of ingestion or contact with the eyes (39).

Exposure to formic acid vapor causes irritation of the eyes and respiratory tract. The TLV/TWA occupational exposure limit is 5 ppm (40). Self-contained breathing apparatus should be used when there is a risk of exposure to high vapor concentrations.

Formic acid is combustible (flash point = 69°C), but the explosive hazard is considered slight. The decomposition to CO requires appropriate precautions to be taken when entering tanks or other confined spaces that have contained the acid.

Formic acid is readily biodegraded, and therefore does not bioaccumulate. The theoretical biological demand (BOD) is 350 mg/g (25).

8. Uses

The largest single use of formic acid is as a silage additive. This market is well developed in Europe, but scarcely exists in the United States. If formic acid is applied to freshly cut grass prior to ensilation, the nutritional value of the ensuing silage is enhanced. Specifically, lactic fermentation is promoted, and the undesirable formation of butyric acid avoided. Milk yields of cattle fed with silage made in this way can be improved through the winter. Mixtures of formic acid with propionic acid or formate salts are also used for this purpose.

Formic acid can also be used as an antisalmonella additive in animal feeds, for decontamination of feed raw materials, and prevention of flock infection in the poultry industry by treatment of the finished feed.

Outside the agricultural area, formic acid finds a range of diverse applications either as an intermediate or as a cost-effective, relatively volatile strong acid. In the textile industry, formic acid is used as an acidulant in the dyeing of both natural and synthetic fibers (see Dyes, application and evaluation). It is also used to neutralize alkaline solutions and facilitate rinsing during laundering. In the leather industry, formic acid finds a number of applications, particularly in tanning (see Leather).

In the rubber industry, formic acid is used for coagulating latex in the production of natural rubber and in the production of certain rubber chemicals (qv) (see Rubber, natural).

Formic acid is used as an intermediate in the production of a number of drugs, dyes, flavors, and perfume components. It is used, for example, in the synthesis of aspartame and in the manufacture of formate esters for flavor and fragrance applications.

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Related Articles

Dyes, application and evaluation; Leather; Rubber, natural