THE MODE OF OXIDATION OF ORGANIC ACIDS

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It is generally known that certain organic acids are readily oxidized, whereas others are decidedly resistant to wet oxidation. This paper is a report of a study made on the relation of oxidizability to the structure and electronic stability of the acid radicals involved. Credit is due Mr. C. S. Moyer and Mr. P. C. Yang, who carried out the experimental side of the investigation.

To the practical chemist, differences in the oxidizability of organic acids are "mere facts," and the mechanism of the reactions concern him very little. The theoretical chemist, on the other hand, regards these differences as highly important, for he uses them in building up his methods of separations and synthesis. The mechanism of the oxidation of organic acids is discussed mainly in terms of formic and oxalic acids. Both of these are recognized as active reducing agents, and yet there are marked differences in the modes of their oxidation. Some of these differences are shown in the following table:

TABLE I.

REACTIONS OF FORMIC AND OXALIC ACIDS

Oxidizing Agent	Reaction with $HCHO_2$	Reaction with $H_2C_2O_4$
O_2 or O_3	H_2CO_3	————
Na_2O_2	$Na_2CO_3 + H_2O$	$Na_2C_2O_4 + H_2O_2$
HNO_3	H_2CO_3	
MnO_2	$Mn(CHO_2)_4$	$Mn^{++} + H_2CO_3$
$HMnO_4$	Slow oxidation	Rapid oxidation (if Mn^{++} is present)
Fehling's solution	Cu_2O	————

Such differences can be explained only in terms of some fundamental differences in the mechanism of the oxidation processes. It appears that formic acid can be directly oxidized by all oxygenating agents, that is, agents that decompose, liberating nascent oxygen. Oxalic acid is unaffected by these agents except in the presence of a suitable catalyst. On the other hand, as is shown later, oxalic acid is oxidized only by linking the oxalate anion to a cation of changeable valence, forming an unstable salt.

The explanation of these differences is found in the electrolytic behavior of formic and oxalic acids. If molar oxalic acid is electrolyzed between electrodes of bright platinum under an increasing potential (fig. 1), there is at first only a slight current with no visible evidence of decomposition. Upon reaching a potential of 0.95 volt, there is
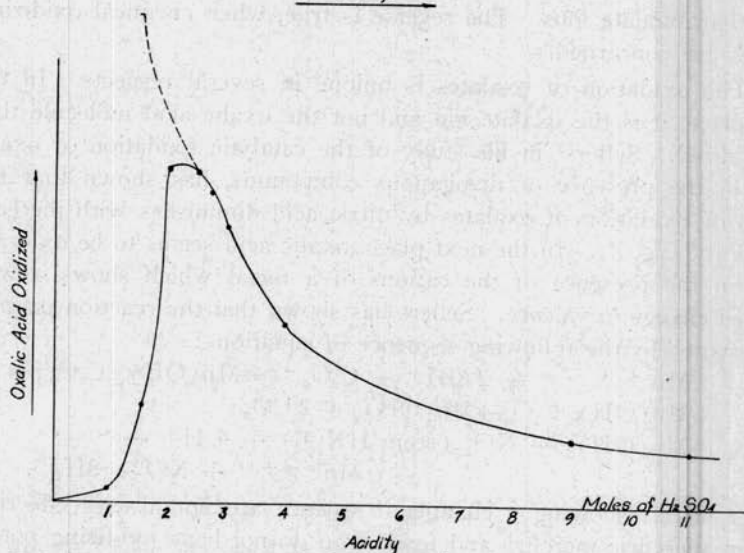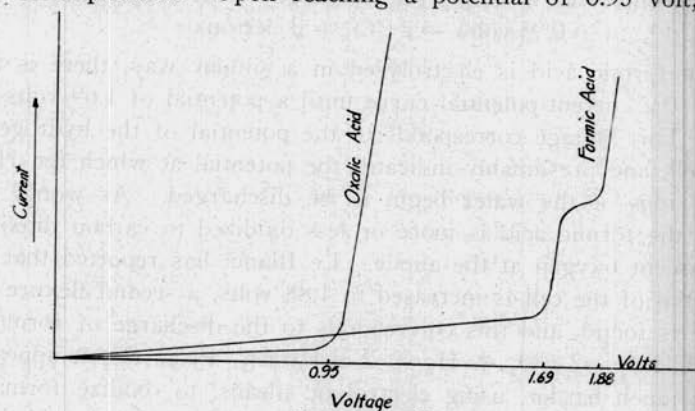

FIG. 1. *(Above)* Decomposition potential curves for formic and oxalic acids.

FIG. 2. *(Below)* Curve showing effect of acidity upon the oxidation of oxalic acid by nitric acid, using Mn as a catalyst.

a rather abrupt increase in current, and carbon dioxide begins to be liberated at the anode. This critical potential of 0.95 volt is called the "decomposition potential" for oxalic acid. This potential is almost exactly the same as the decomposition potential of hydrobromic acid.

This would call for the displacement of the oxalate group by chlorine, just as the bromine ion is displaced, and this is exactly the case:
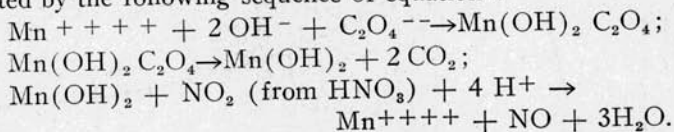
$$2\,Br^- + Cl_2 \rightarrow Br_2 + 2\,Cl^-;$$
$$C_2O_4^{--} + Cl_2 \rightarrow 2\,CO_2 + 2\,Cl^-.$$
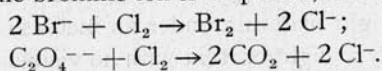
The reaction involved is simply the discharge of the oxalate anion:

$$C_2O_4^{--}(+0.95\ volt) \rightarrow 2\,CO_2 + 2\ elctrons.$$
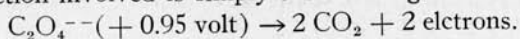
When formic acid is electrolyzed in a similar way, there is no flexure in the current-potential curve until a potential of 1.69 volts is reached. This voltage corresponds to the potential of the hydrogen-oxygen cell, and presumably indicates the potential at which the H^+ and OH^- ions of the water begin to be discharged. As would be expected, the formic acid is more or less oxidized to carbon dioxide by the nascent oxygen at the anode. Le Blanc[1] has reported that if the potential of the cell is increased to 1.88 volts, a second flexure in the curve is found, and this corresponds to the discharge of formate ions: $2\,CHO_2^- \rightarrow 2\,CO_2 + H_2 + 2$ electrons. From this it appears that it is much harder, using electrolytic means, to oxidize formate ions than oxalate ions. The reverse is true, when chemical oxidizing agents are concerned.

The oxidation of oxalates is unique in several respects. In the first place, it is the oxalate ion and not the oxalic acid molecule that is oxidized. Sellers[2] in his study of the catalytic oxidation of oxalic acid in the presence of manganous compounds, has shown that the speed of oxidation of oxalates by nitric acid diminishes with increase in acidity (fig. 2). In the next place, oxalic acid seems to be oxidized only in the presence of the cations of a metal which shows a well defined change in valence. Sellers has shown that the reaction may be represented by the following sequence of equations:

$$Mn^{++++} + 2\,OH^- + C_2O_4^{--} \rightarrow Mn(OH)_2\,C_2O_4;$$
$$Mn(OH)_2\,C_2O_4 \rightarrow Mn(OH)_2 + 2\,CO_2;$$
$$Mn(OH)_2 + NO_2\ (from\ HNO_3) + 4\,H^+ \rightarrow$$
$$Mn^{++++} + NO + 3H_2O.$$

Other metals showing a change of valence are not always effective. Silver, mercuric mercury and ferric iron do not have oxidizing potentials high enough, and tetravalent lead in the form of lead dioxide is too insoluble in weak acid solution to form an oxalate. Next to manganese, vanadium seems to be the most suitable catalyst.

The oxidation of formates is in every respect similar and parallel to the oxidation of aldehydes. (See Table II.) Since both contain the CHO-group, the mechanism is clearly characteristic of this radical.

[1] Zeit. phys. Chem., vol. 8, p. 299, 1891.
[2] Thesis, University of Illinois, 1929.

TABLE II

REACTIONS OF FORMIC ACID AND ALDEHYDES WITH OXIDIZING AGENTS

Oxidizing Agent	Reaction with HCOOH	Reaction with CH_3CHO
O_2	H_2CO_3	CH_3COOH
$Ag(NH_3)_2OH$	Ag deposit	Ag deposit
Fehling's Soln.	Cu_2O	Cu_2O
HgO	$Hg + H_2CO_3$	$Hg + CH_3COOH$

Both the formic acid molecule and the formate ion are good reducing agents. Several mechanisms have been suggested to explain the oxidation of the aldehyde group. Wieland[3] has studied the oxidation of aldehydes very extensively and proposed several mechanisms to explain them. In 1912 he suggested the idea that the aldehyde was first hydrated, and then hydrogen split out as follows:

$$RCHO + H_2O \rightarrow RCH(OH)_2 \rightarrow RCOOH + H_2.$$
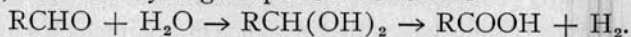
In 1921 he advanced the theory of the formation of peracids as intermediate in the oxidation process. More recently, in 1923, he proposed a peroxide theory, which has been very favorably received. According to this theory, oxygen is added to the carbonyl group, forming a peroxide, followed by the migration of the H atom:

$$2\ RCHO + O_2 \rightarrow 2\ RCH(O_2) \rightarrow 2\ RCOOH.$$

While other representatives of the more common organic acids have not yet been thoroughly studied, some general statements may be made in regard to their behavior. Acetic, succinic and similar acids are known to be very resistant to wet oxidation, being only slowly affected by such strong oxidizing agents as permanganic and chromic acids. Under such drastic oxidation, only the final products, carbon dioxide and water, can be identified. Tartaric and citric acid are fairly active reducing agents, with decomposition voltages only slightly less than that of water. This indicates that their oxidation is due to nascent oxygen, just as in the case of formic acid.

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[3] Ber. 45, II, 2606-15 (1912) ; ibid. 54B, 2353-76 (1921) ; Ann. 431, 301-22 (1922).