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Palladium (II)-Catalyzed Oxidation of Formic Acid in Acetic Acid Solution*

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The oxidation of formic acid to carbon dioxide and water in acetic acid–lithium acetate solution with palladium(II) catalysts was studied. The reaction was carried out in the presence of cupric salts and oxygen to reoxidize elementary palladium: (1) $HCOOH + Pd(II) \rightarrow CO_2 + Pd^0 + 2H^+$; (2) $Pd^0 + Cu(II) \rightarrow Cu(I) + Pd(II)$; (3) $2Cu(I) + 2H^+ + \frac{1}{2}O_2 \rightarrow 2Cu(II) + H_2O$. Under conditions in which the reaction represented by Eq. (1) was rate-determining the reaction rate was directly proportional to formic acid, palladium(II) concentration and approximately directly proportional to lithium acetate concentration. With excess lithium acetate the rate expression became zero order in acetate: $-d[HCOOH]/dt = k\,[Pd(II)]\,[HCOOH]$ and k was found to be 0.12 1 mole^{-1} sec^{-1} at 112°C. From the variation of k with temperature, values of $\Delta H^\ddagger = 22$ kcal mole^{-1} and $\Delta S^\ddagger = -6$ cal mole^{-1} deg^{-1} were calculated. The deuterium isotope effect for DCOOH was determined to be $k[H]/k[D] = 2.0$ at 112°C.

A mechanism is proposed in which the rate-limiting step is the decomposition of a palladium(II)-formate complex. This complex decomposes either via a two-electron transfer from the coordinated formate ion coupled with proton loss, or via a palladium(II) hydride complex which then decomposes rapidly. Similar mechanisms had been proposed by other authors for the oxidation of formic acid with thallium(III), mercury(II), and mercury(I).

INTRODUCTION

The decomposition of formic acid, being a simple reaction, has been studied by many workers interested in the fundamental aspects of heterogeneous catalysis (*1*). The oxidation of formic acid in solution by many different substances also has been investigated extensively. The oxidation by palladium(II) has been mentioned in the patent literature (*2*). Also it has been reported that some phosphine complexes of palladium(II) and other Group VIII metals decompose formic acid in acetic acid solutions (*3*). The kinetics of the reactions were not investigated. In the course of our studies (*4*) of the oxidation of olefins by palladium(II) we became interested in the kinetics of the reaction of formic acid with this metal ion and in comparing our results with those reported for thallium(III) and mercury(II) (*5, 6, 7*). These three metal ions show some similarities in their reactions with olefins (*8, 9, 10*). In this paper, a kinetic study of the oxidation of formic acid-catalyzed by palladium(II) in acetic acid–lithium acetate solution is presented. The reaction was studied in the presence of cupric salts and oxygen which served to reoxidize elemental palladium (*4*).

EXPERIMENTAL

Reagents. Palladous chloride was purchased as a solution (about 1.8 *M*) in aqueous hydrochloric acid (about 0.6 *M* in HCl). The stock solution was prepared by diluting 20 ml of the aqueous solution to 1000 ml with glacial acetic acid. It was analyzed for palladium(II) (atomic absorption) and for total chloride (precipitation of silver chloride). The composition of the stock solution was (in mole per liter):

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palladium(II), 0.0345; total chloride, 0.171; hydrochloric acid (calculated), 0.1025. Oxygen was purchased from Big Three Industrial Gas and Equipment Co. In the runs in which the total formic acid and formate concentration was determined by radioanalyses, ^{14}C sodium formate from New England Nuclear was used; 0.8 g of sodium formate (500 μCi) was dissolved in 200 ml of reagent grade formic acid. An aliquot of this solution (1 to 5 ml) was used in each experiment to obtain a catalyst solution with about 20.000 dpm/g. The deuteroformic acid (DCOOH) was obtained from Merck, Sharp and Dohme of Canada, Limited and it had a minimum isotopic purity (atom % D) of 99%. All other chemicals were reagent grade.

Equipment and experimental procedure. The experiments were made using 500 ml of the catalyst solution (the composition is given in Table 1) at 40 psig of pressure ($O_2 + CO_2$ produced) and in general at 112°C. The equipment used consisted of a 700-ml glass-jacketed reactor (2 inches in diameter) containing the catalyst solution into which oxygen was bubbled through a fritted glass sparger. The effluent gases passed through a condenser and a trap immersed in Dry Ice-acetone and were metered and analyzed for carbon dioxide and oxygen. The oxygen flow was adjusted to obtain an effluent flow of about 100 ml/min. Analyses of the formic acid in the reactor liquid were made every hour on small aliquots (<1 ml) and analyses of the vent gas were made every hour on samples of 1000 ml, collected during 10 min. The catalyst solution was first prepared without the addition of formic acid or palladium(II). Formic acid and the calculated amount of palladium(II) stock solution were added only after all the salts had dissolved and the solution was at a temperature of 112°C. At this moment a sample was taken as a reference for radioanalysis. The solution then was introduced into the reactor (using vacuum). The temperature was adjusted to 112°C and the pressure to 40 psig with oxygen. At this moment, a sample was taken from the reactor. This was considered to be the starting time of the run. The composition of the catalyst solutions used in the different experiments is presented in Table 1. The values of total chloride include the chloride added with the stock solution of palladium(II). The values of lithium acetate are corrected for the small amount that formed lithium chloride by reaction with the hydrochloric acid of the stock solution of palladium(II). In the majority of the experiments on formic acid decomposition the palladium(II) concentration of the catalyst solution was 0.5×10^{-3} mole/liter. As a consequence the contribution from the palladium(II) stock solution to the final catalyst solution was only 2×10^{-3} mole/liter of chloride and 1.5×10^{-3} mole/liter of hydrochloric acid.

Analytical procedures. The carbon dioxide and oxygen in the vent were de-

TABLE 1

COMPOSITION OF THE CATALYST SOLUTION[a]

Experiments for the determination of—	Initial concentration (mole l^{-1})					
	CH_3COOLi	$(CH_3COO)_2Cu$	Total chloride	H_2O	$Pd(II) \times 10^{-3}$	HCOOH
Stoichiometry	2.0	0.3	0.12	1.1	0.5	1.2
Effect of formate concentration	2.0	0.3	0.12	1.1	0.5	1.2
Effect of palladium(II) concentration	2.0	0.3	0.12	1.1	Variable	1.2
Effect of acetate concentration	Variable	0.3	0.12	5.0	0.5 and 1.0	0.6 and 1.2
Effect of chloride concentration	1.0	0.3	Variable	5.0	0.5 and 1.0	1.2
Effect of copper(II) concentration	1.0 to 1.6	Variable	0.12	5.0	0.5	1.2
Effect of temperature	1.0	0.3	0.12	5.0	1.0	0.6
Deuterium isotope effect	1.0	0.3	0.12	5.0	0.5	0.6

[a] In all the experiments the solvent was acetic acid, the total pressure 40 psig and the temperature 112°C (except when the effect of temperature was studied).

termined by mass spectrometry. The formic acid in the liquid was determined by radioanalysis of the ^{14}C-formic acid. The samples were counted on a Packard-Tricarb liquid scintillation counter. In the runs with DCOOH its concentration was determined by gas chromatographic analysis of the methyl ester, which was formed by reaction with 2,2-dimethoxypropane. This analytical procedure was also used for some of the samples from other runs. The results were in good agreement with those obtained by radioanalyses.

RESULTS AND DISCUSSION

Preliminary experiments with solutions of palladium chloride in acetic acid (in the absence of copper salts) showed that formic acid reduced palladium(II) to elemental palladium only when some acetate was present (e.g., lithium acetate). In the absence of lithium acetate (1.5×10^{-3} mole/liter of hydrochloric acid) the solution of palladium(II) and formic acid was stable at 112°C for at least 3 hr. The experiments indicate that as in the case of thallium(III) and mercury(II) (*7*), formate ion rather than formic acid was the reacting species. The experiments also showed that elemental palladium, which agglomerated rapidly, did not have any significant catalytic effect on the formic acid decomposition.

To avoid changes in the composition of the solution during the experiments, the formic acid oxidation was studied using palladium(II) as a catalytic agent only. It is well known (*4*) that elemental palladium can be reoxidized rapidly by copper(II) salts (e.g., acetate) in the presence of some chloride ion and also that the copper(I) salts formed can be reoxidized to the copper(II) state with oxygen (*11, 12*). By carrying out the formic acid oxidation with palladium(II) in the presence of copper(II) salts and oxygen and under conditions in which the reaction represented by Eq. (1) was rate-determining (absence of elemental palladium and/or cuprous chloride precipitation) it was possible to study the kinetics of this reaction with only catalytic amounts of palladium:

$$\mathrm{HCOOH} + \mathrm{Pd(II)} \rightarrow \mathrm{CO_2} + \mathrm{Pd^0} + 2\mathrm{H^+} \qquad \text{Formic acid oxidation} \qquad (1)$$

$$\mathrm{Pd^0} + 2\mathrm{Cu(II)} \rightarrow \mathrm{Cu(I)} + \mathrm{Pd(II)} \qquad \text{Palladium oxidation} \qquad (2)$$

$$2\mathrm{Cu(I)} + 2\mathrm{H^+} + \tfrac{1}{2}\mathrm{O_2} \rightarrow 2\mathrm{Cu(II)} + \mathrm{H_2O} \qquad \text{Cuprous oxidation} \qquad (3)$$

$$\mathrm{HCOOH} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \qquad \text{Overall reaction} \qquad (4)$$

Control experiments in the absence of palladium(II), showed that copper acetate and lithium salts did not decompose formic acid under the conditions studied.

Stoichiometry of the reaction. By comparing the rate of formic acid decomposition with the rate of carbon dioxide formation it was determined that about 1.1 mole of CO_2 was formed per mole of formic acid decomposed. The 10% excess of CO_2 over the stoichiometric amount can be attributed to acetic acid decomposition. The rate of carbon dioxide production by a similar catalyst solution in the absence of formic acid does not account for all of the excess of carbon dioxide. However, the presence of formic acid could induce acetic acid degradation by producing copper(I) [Eqs. (1) and (2)], which must be reoxidized with oxygen [Eq. (3)]. This reoxidation produces peroxides and free radicals (*11, 12*) that could attack the solvent. Production of carbon dioxide from acetic acid during the formic acid decomposition by complexes of Group VIII metals has been observed before (*3*).

Effect of formic acid concentration. In the presence of copper(II), lithium acetate, and lithium chloride a plot of the log of total formate concentration (as determined by radioanalysis) as a function of time was linear, indicating a first order dependence on total formate concentration. From this plot the pseudo-first-order reaction constant k' was determined under different conditions to determine the effect of the other variables.

Effect of palladium(II), total acetate,

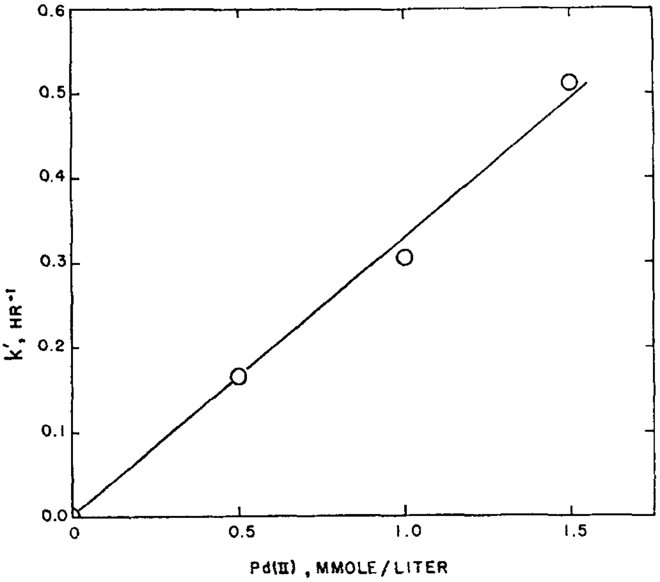


FIG. 1. Effect of Pd(II) concentration on the rate of formic acid oxidation.

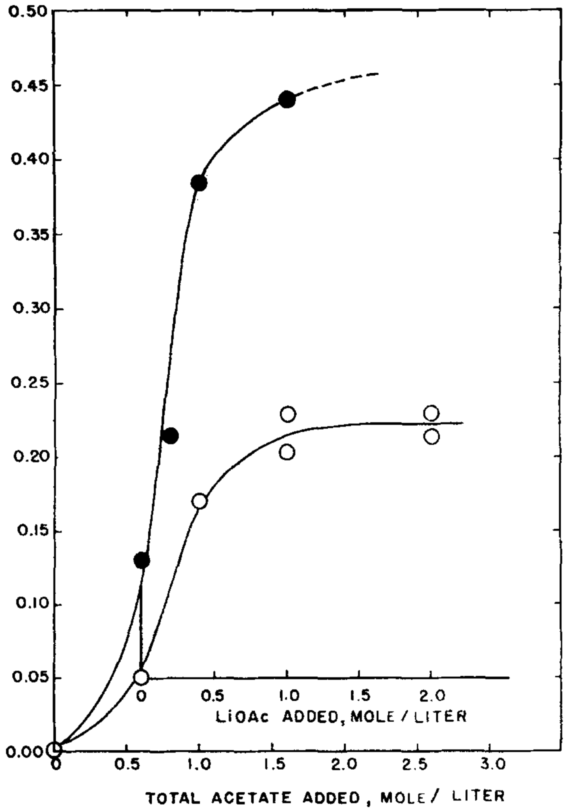


FIG. 2. Effect of acetate concentration on the rate of formic acid oxidation: ○: HCOOH, 1.17; Pd(II), 0.5×10^{-3}; ●: HCOOH, 0.58; Pd(II), 1.0×10^{-3}.

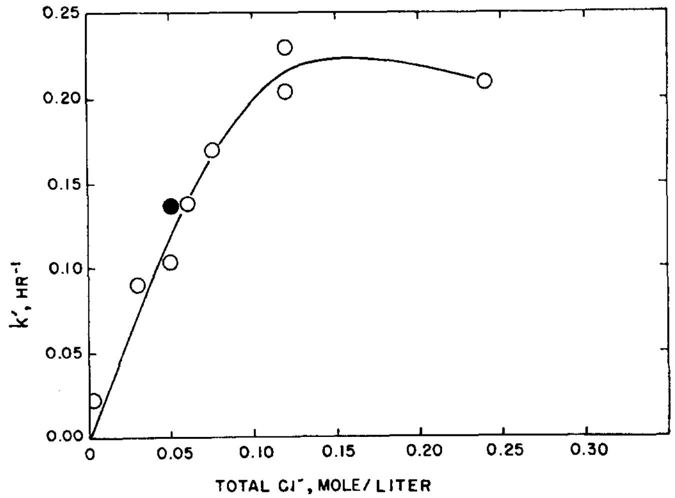


FIG. 3. Effect of total chloride concentration on the rate of formic acid oxidation: Pd(II), 0.5×10^{-3}; Pd(II), 1.0×10^{-1} (mole l^{-1}).

total chloride, and copper(II). The effects of these components of the catalyst solution were studied by plotting the pseudo-first-order reaction constant k' as a function of the concentration of each of the components. The results are presented in Figs. 1 through 4. The reaction is first order in palladium(II) and approximately first order in acetate up to a limiting case in which it becomes zero order in acetate. In the study of these two variables, the chloride and copper(II) concentration as well as the oxygen pressure were high enough to make some of the steps of the reaction represented by Eq. (1) rate-determining. As a consequence precipitation of elemental palladium and/or cuprous salts was never observed. The effect of palladium(II) and lithium acetate strongly indicates the formation of a palladium(II) formate complex as the reaction intermediate. The smaller effect of copper(II) acetate on the rate of oxidation as compared

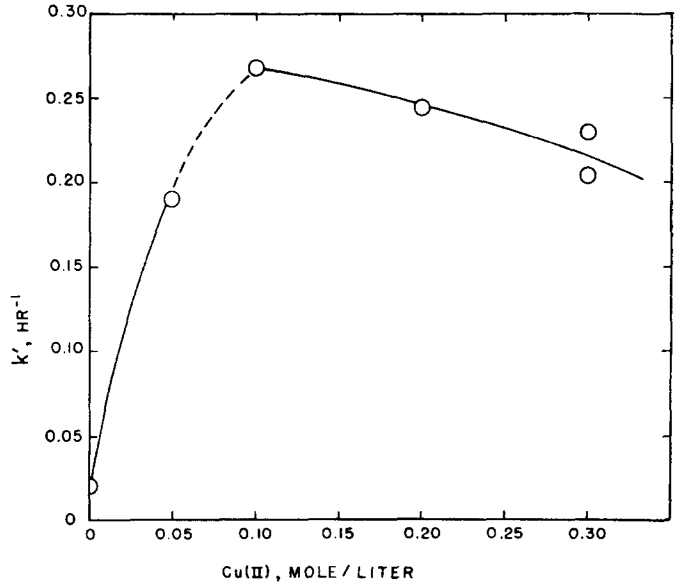


FIG. 4. Effect of Cu(II) concentration on the rate of formic acid oxidation.

to lithium acetate (indicated by the initial part of the curves in Fig. 2) can be explained by the stronger tendency of copper(II) to complex with acetate. Also, at a high acetate level, either all of the formate is present as the anion or all of the palladium(II) is present as the formate complex. As a consequence, the reaction becomes pseudo zero order in acetate, as indicated in the last part of the curves in Fig. 2.

When the effect of chloride and copper(II) ions was studied, the experiments presented in the first ascending part of the curves (Figs. 3 and 4) were characterized by precipitation of elemental palladium at the beginning of the run. Addition of more palladium(II) resulted in more precipitation of elemental palladium without any significant increase in rate. In these experiments the palladium reoxidation [Eq. (3)], probably was rate-limiting and elemental palladium precipitated until the rate of palladium formation [Eq. (1)], equaled the rate of reoxidation [Eq. (2)]. As it is known that the rate of palladium reoxidation with copper(II) salts increases with both the copper(II) and the chloride concentration (*4*) one would expect an increase in the overall rate (as shown in Figs. 3 and 4) when increasing the concentration of these ions. In the experiments represented in the second part of the curves, palladium precipitation was not observed and the reaction represented by Eq. (1) was probably rate-limiting. This second part of the curve represents the effect of these variables on the formic acid acid oxidation by palladium(II) [Eq. (1)]. It can be seen that chloride ion has little or no effect on the reaction. Copper(II) decreases the rate slightly. This can be explained by a decrease of the effective formate ion concentration, due to copper(II) complexation with formate or acetate ion or both. The important fact is that, in the formic acid oxidation by palladium(II), copper(II), has no synergistic effect such as has been observed in other reactions in acetic acid catalyzed by palladium(II) (*4, 13*).

Effect of temperature and experiments with DCOOH. From the variation of k' with temperature (from 100° to 125°C), values of $\Delta H^\ddagger = 22$ kcal mole^{-1} and $\Delta S^\ddagger = -6$ cal mole^{-1} deg^{-1} were calculated. Experiments with DCOOH indicated a deuterium isotope effect of 2.0 at 112°C. The enthalpy of activation is close to the values reported for thallium(III) and mercury(II) oxidation of formic acid (*5*). The deuterium isotope effect is also of similar magnitude to those reported for these ions if one considers the difference in temperature of the experiments. The entropy of activation has been shown to be associated largely with equilibria prior to the rate-limiting decomposition of the formate-thallium(III) ion (*5*). In the palladium(II) oxidation, the negative $\Delta S^\ddagger$ value could indicate that one of these preequilibria involves the reaction of ions of the same sign (*14*).

Mechanistic considerations. The palladium(II) species present in glacial acetic solutions are not known. For simplification we will represent the predominant palladium ion as monomeric, although dimeric species cannot be ruled out. We will use the representation PdL_4, in which L is any ligand such as acetate, chloride, or acetic acid. Since the charges on the individual species will vary accordingly, we will not attempt to balance these charges in the equations used in the mechanism. Also it is well known the conductivity of electrolytes, even that of the strong ones, is very low in acetic acid (*15*). This indicates that they probably exist as neutral molecules or ion pairs. For this reason the species in solution should perhaps be represented as undissociated. However, we will use the ionic representation for the sake of simplification.

The experimental data can be explained using the following sequence of elementary steps to represent Eq. (1):

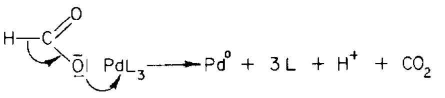
$$HCOOH + CH_3COO^- \rightleftharpoons HCOO^- + CH_3COOH \qquad (5)$$

$$PdL_4 + HCOO^- \rightleftharpoons HCOOPdL_3 + L \qquad (6)$$

$$HCOOPdL_3 \xrightarrow[AcO^-]{AcOH} Pd^0 + 3L + H^+ + CO_2 \qquad \text{slow} \qquad (7)$$

Probably the ligand replaced in the reaction represented in Eq. (6) is acetic acid solvent since no significant inhibition by chloride or acetate ion was found. Alternatively, instead of replacement of a ligand, the reaction could be one in which formate ion opens a bridge in a dimeric species. The reaction represented in Eq. (7) in which in the rate-limiting step a hydrogen–carbon bond is broken is in agreement with the experimental deuterium isotope effect. Also it is easy to see that according to this mechanism the reaction will be first order in palladium(II), formic acid, and acetate ion. It will become pseudo zero order in acetate ion concentration when all the formic acid is present as formate ion or all the palladium(II) is present as the formate complex: $-d[\mathrm{HCOOH}]/dt = k[\mathrm{Pd(II)}]$ [HCOOH]. The value of k at 112°C was determined to be 0.12 l mole^{-1} sec^{-1}.

The formate complex may decompose through a two-electron transfer from the coordinated formate ion to the palladium(II). This transfer is coupled with proton loss to solvent or to an acetate of the coordination sphere.



$$\mathrm{HCOO\,PdL_3} \longrightarrow \mathrm{Pd^0} + 3\mathrm{L} + \mathrm{H^+} + \mathrm{CO_2} \quad (8)$$

In this reaction $\mathrm{Pd^0}$ could be an unstable zerovalent complex of palladium with the ligands (*4*).

This mode of decomposition has been proposed by Halpern and Taylor (*5*) for the formic acid oxidation by thallium(III), mercury(II), and mercury(I). Alternatively, a hydride transfer to palladium(II) with subsequent rapid decomposition of the palladium hydride cannot be ruled out. Hydride complexes of iridium have been isolated when formic acid has decomposed in acetic acid solutions by $[\mathrm{Ir\,Cl\,CO(PPh_3)_2}]$ (*3*). Successive one-electron transfer reactions have been considered improbable (*5*) for thallium(III), mercury(II), and mercury(I) and it will be difficult to explain the kinetics and deuterium isotope effect in the palladium(II)-catalyzed reaction with this type of mechanism. Finally we must mention that iridium(III) and rhodium(III) carbonyl complexes have been obtained by the reaction of formic acid with iridium(III) and rhodium(III) salts (*3*, *16*). This type of intermediate cannot be ruled out for the palladium(II)–formate reaction, especially since such complexes have been proposed as intermediates in the palladium(II)-catalyzed oxidation of carbon monoxide (*17*).

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