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Catalytic Oxidation of Glyoxal to Glyoxylic Acid on Platinum Metals

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Aqueous solutions of glyoxylic acid (CHOCOOH) have been prepared by catalytic oxidation of aqueous glyoxal (CHOCHO) solution with air slightly above room temperature. The catalysts are carbon-supported platinum metals. Provided the pH is regulated near neutrality, the yield of glyoxylic acid (GLY) can be as high as 70% at 85.5% glyoxal conversion. GLY is subsequently oxidized quantitatively into oxalic acid. The oxidation mechanism probably involves an end-on adsorption of the glyoxal dihydrate molecule on the metal surface followed by dehydrogenation. The initial rate of GLY formation increases in the series $0 = \mathrm{Ru} < \mathrm{Rh} < \mathrm{Pd} < \mathrm{Ir} < \mathrm{Pt}$, similar to the series of the redox potentials of these elements. Ruthenium is totally inactive because it is probably covered with hydroxyl groups that catalyze side reactions such as dismutation (Cannizzaro reaction) and direct oxidation of glyoxal into formic acid (C–C bond rupture).

INTRODUCTION

Glyoxylic acid (CHOCOOH) is a highly reactive synthon entering into the preparation of a number of fine chemicals such as those manufactured by the perfume and flavor industry and by the pharmaceutical industry. It is prepared industrially by various routes, including oxidation of aqueous solutions of glyoxal (CHOCHO) with nitric acid (*1, 2*). Different attempts have been made to prepare glyoxylic acid by electrocatalytic oxidation of glyoxal (*3–7*). The best yields (70%) were obtained in hydrochloric (3) or perchloric (7) acid solutions; however, with hydrochloric acid the evolution of chlorine at the anode limits the potential interest of the electrochemical process. The present work is, to our knowledge, the first attempt to use metal catalysts and air to oxidize glyoxal into glyoxylic acid selectively. Although Davy (*8*) showed 170 years ago that ethanol is converted to acetic acid on platinum there are comparatively few studies on the liquid phase oxidation of oxygenated compounds on metal catalysts. The first major contributions to this subject were from Heyns and Blazejewicz (*9*), Heyns and Paulsen (*10*), and Ioffe *et al.* (*11, 12*). However, interest in the subject rose during the past decade especially for metal-catalyzed oxidation of carbohydrates to produce a variety of valuable chemicals. Review papers on carbohydrate oxidation have been published recently (*13–15*).

The selective oxidation of glyoxal is a tough challenge for a number of reasons. Glyoxal in aqueous solution takes different oligomeric forms (*16*) in equilibrium with the monomeric dihydrate $\mathrm{CH(OH)_2CH(OH)_2}$, which is expected to be the reactive species; the lower the concentration and the higher the pH, the higher the fraction of the monomer. However, the concentration of glyoxal in solutions should not be kept too low for the economy of an industrial process and the pH should not be kept too high since glyoxal could dismute into glycolic acid ($\mathrm{CH_2OHCOOH}$) via the Cannizzaro reaction.

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The main pitfall is the overoxidation of the molecule leading to oxalic acid and even to carbon dioxide. Indeed, there is a high probability for a simultaneous or successive oxidative dehydrogenation of the two functional groups of the molecule before it desorbs from the metal surface.

The present work was intended to compare the activities and selectivities of different platinum metals. Since the question of metal specificity is addressed, all the catalysts have been prepared on the same support and with similar metal dispersion.

EXPERIMENTAL

Catalysts

The starting material was an active charcoal prepared by physical activation of pine wood (CECA 50S); most particles are within 0.1–1 μm and the BET area is 1400 $m^2\ g^{-1}$. Mineral impurities were eliminated by refluxing 50 g of active charcoal suspended in 500 ml of HCl solution (2 mol $liter^{-1}$) for 24 h. After washing with water until the wash waters were neutral, the active charcoal was dried and submitted to partial combustion at 500°C in air for 3 h. Then it was oxidized in a solution of sodium hypochlorite (15% active chlorine) stirred for 24 h. The suspension was filtered, washed with hydrochloric acid to eliminate the excess of NaClO, and finally thoroughly washed with water until the wash waters were Cl-free. The number of acidic groups titrated by NaOH increased from 0.35 to 1.15 mmol m^{-2} after the oxidation treatment.

The platinum catalyst Pt/C was prepared by the method described by Dirkx and van der Baan (*17*). An aqueous solution of hexachloroplatinic acid (1 g $H_2PtCl_6,6H_2O$ in 20 ml H_2O) was added to 7 g of the oxidized active charcoal. The suspension was stirred for 5 h at room temperature while nitrogen was bubbled through. After cooling to 0°C, 18 ml of a 37% formaldehyde solution was added to the suspension and 10 min later three successive additions of 3 ml of 30% KOH solution were made. After stirring the mixture overnight, the catalyst was filtered and washed until the wash waters were neutral. The catalyst was dried under vacuum at 100°C. Active charcoal-supported palladium, iridium, rhodium, and ruthenium catalysts were prepared by ion exchange of the acidic groups of the oxidized active charcoal with $Pd(NH_3)_4^{2+}$, $Ir(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5Cl^{2+}$, and $Ru(NH_3)_6^{2+}$ cations, respectively: details of the preparation conditions were given previously (*18–21*). The ion-exchanged solids were reduced under flowing H_2 at 573 K to obtain the Pd/C, Ir/C, Rh/C, and Ru/C catalysts. The composition of the catalysts determined by chemical analysis are given in Table 1.

The size of the metal particles and their distribution in the grains of microporous active charcoal were determined by transmission electron microscopy (TEM) with a JEOL 100 CX microscope. Thin sections were cut with an ultramicrotome to check whether the metal particles were distributed throughout the charcoal grain.

Reaction Procedure

Glyoxal solutions were oxidized batchwise with air at atmospheric pressure in a 500-ml thermostated glass reactor equipped with a stirrer, a thermometer, a pH electrode, and ports for gas inlet, gas outlet, and liquid sampling. The pH was regulated with a pH meter controlling the injection of calibrated volumes of KOH solution to neutralize the acids formed. Glyoxal solutions and catalysts were loaded into the reactor and stirred for 90 min under nitrogen. As air was bubbled at 100 ml min^{-1} through the well-stirred solution, the oxidation reaction started immediately (time zero). Glyoxal oxidation was monitored by the volume of KOH solution consumed to neutralize the acidity; however, since different oxidation products were formed, the KOH consumption gave only qualitative information on catalyst activity. Reaction rate and product distribution were measured by HPLC analysis of aldehydes and acids in samples of the reaction medium taken from the reactor at various time intervals. Aldehydes were con-

TABLE 1

Characterization of Catalysts

Catalyst	Type of preparation[a]	wt % metal	Particle size[b] (nm)
Ru/C	1	4.6	<1
Rh/C	1	2.7	2–3(2.5)
Pd/C	1	4.0	1.5–2(1.7)
Ir/C	1	2.9	1.5–2(1.7)
Pt/C	2	4.2	1.5–2(2.0)

[a] (1) Ion exchange and H_2 reduction; (2) H_2PtCl_6 adsorption and formaldehyde reduction (see text).

[b] Determined by TEM on ultramicrotome sections (average size in parentheses).

verted to oximes with *o*-(4-nitrobenzyl) hydroxylamine hydrochloride. The oximes were then determined by HPLC with xylene as internal standard on a Nucleosil C14 column. The acids were determined directly after separation on a Biorad HPX 87H column.

RESULTS AND DISCUSSION

1. Characterization of Catalysts

The compositions of the catalysts are given in Table 1. Previous TEM studies (*19–21*) have shown that all the catalysts prepared by ion exchange of the oxidized active charcoal (Ir/C, Pd/C, Rh/C, and Ru/C) present a very high and homogeneous metal dispersion. The particle sizes are in the range given in Table 1.

Catalyst Pt/C prepared by adsorption of $PtCl_6^{2-}$ ions on the oxidized active charcoal and reduction with formaldehyde is also very well dispersed. Figure 1 is a TEM view through an ultramicrotome thin section of Pt/C; metal particles are in the size range 1.5–2 nm. Examination of several sections show that the particles are distributed homogeneously throughout the charcoal grains. The main advantage of using the formaldehyde reduction technique is that large amounts of catalyst can be prepared with all steps carried out in the liquid phase. In contrast, metal catalysts obtained by hydrogen reduction should be prepared in small batches to avoid inhomogeneity in the final metal dispersion and great care should be exercised to avoid deep metal oxidation when the catalyst is transferred from the reduction cell to the reactor.

2. Reactions without pH Regulation

A few preliminary experiments were carried out on Pt/C catalysts without any pH regulation. Starting from a concentrated (3 *M*) glyoxal solution and with a glyoxal to platinum molar ratio of 5674, the oxidation conducted at 33°C was slow and led essentially to carbon dioxide. The oxidation at 44°C of more dilute glyoxal solution (0.1 *M*, glyoxal/Pt = 169) gave oxalic acid (OX) (maximum yield 43%, pH 1.2) then the diacid was converted to carbon dioxide (final pH 5.9). Glyoxylic acid (GLY) was not detected in the liquid phase but can appear transiently as an adsorbed surface intermediate. The overall reaction pathway could be described by the following tentative scheme where the adsorbed species are within square brackets.

$$\begin{tikzcd}
\mathrm{(OH)_2HC{-}CH(OH)_2} \arrow[d, shift left] & & & \\
\mathrm{[(OH)_2HC{-}CH(OH)_2]} \arrow[u, shift left] \arrow[r] & \mathrm{[(OH)_2HC{-}COOH]} \arrow[r] & \mathrm{[HOOC{-}COOH]} \arrow[r] \arrow[d, shift left] & \mathrm{[CO_2]} \arrow[d] \\
& & \mathrm{HOOC{-}COOH} \arrow[u, shift left] & \mathrm{CO_2}
\end{tikzcd}$$

There is no hope of obtaining significant amounts of glyoxylic acid because it remains bonded to the surface. Indeed carboxylic acids are strongly bonded on metal surfaces in the form of carboxylates. For instance, the heat of formation of platinum formate is as high as 318 kJ mol^{-1} (*22*). It is clear that desorption of acids from the metal surface must be promoted to obtain GLY in the liquid phase.

3. Oxidation on Platinum Catalyst

The simplest way to favor the desorption of acids from the surface is to carry out oxidation reactions at higher pH values in

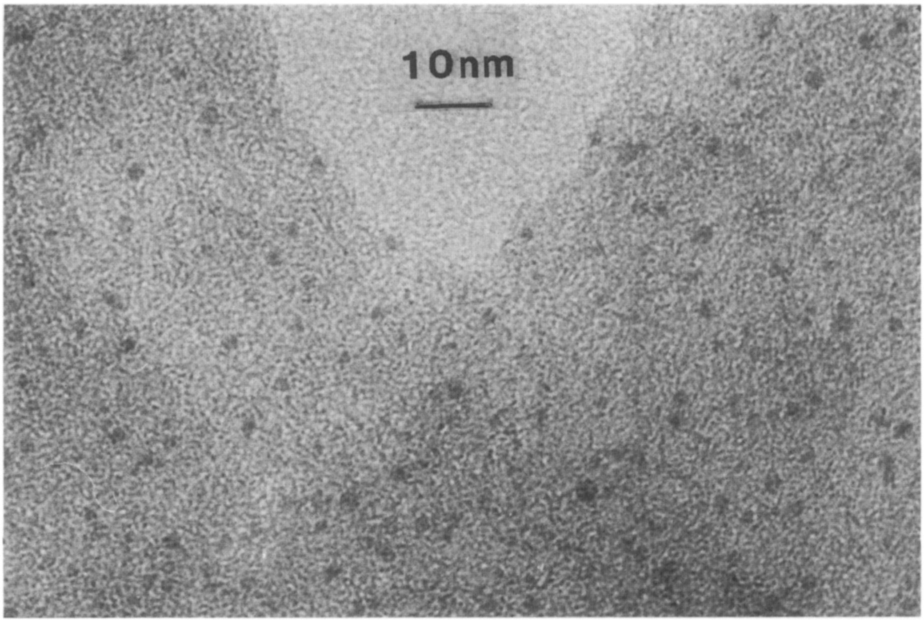


FIG. 1. TEM view through an ultramicrotome section of a grain of Pt/C catalyst.

alkaline solutions so that the adsorbed species tend to leave the surface to form glyoxylate salts in the liquid phase. However, even in weak basic solution, glyoxal is quantitatively disproportionated into glycolic acid (*23*). To determine the highest pH value at which the Cannizzaro reaction occurs at a negligible rate, oxidation reactions were performed in the absence of catalyst at different pH values. These blank experiments indicate that under our experimental conditions no glycolic acid is detected at pH values smaller than 7.9 and that glyoxal is not oxidized, which means that there is no autoxidation via a radical-type mechanism. All the catalytic oxidations were subsequently carried out at a constant pH of 7.7.

The oxidation of a 0.1 *M* glyoxal solution was conducted at 38°C on the Pt/C catalyst with a molar ratio glyoxal/platinum = 177. Only GLY and OX were detected by HPLC in the reaction medium. The product distribution is given in Fig. 2 as a function of time. Slight amounts of GLY and OX appeared after stirring the glyoxal solution for 90 min under a nitrogen atmosphere. They were probably produced by glyoxal oxidation with oxygen adsorbed on the catalyst and dissolved in the solution. Once air was admitted, glyoxal was oxidized essentially to GLY; then after 55 min, substantial amounts of OX were formed. A maximum in GLY yield $(\mathrm{GLY})_\mathrm{M}$ = 60% was obtained at t_M = 79 min and for a glyoxal conversion C_M = 85.5%; thus the glyoxal selectivity was S_M = 70% (Table 2). OX was formed mainly

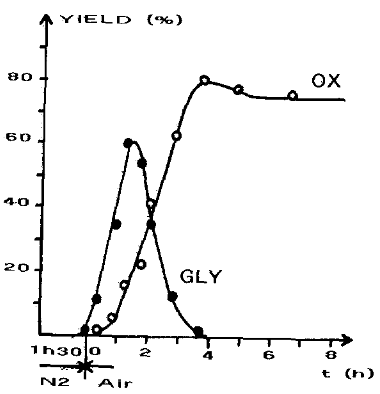


FIG. 2. Product distribution obtained by glyoxal oxidation with air on a Pt/C catalyst as a function of time (38°C, pH 7.7, [GLY] = 0.1 mol liter^{-1}, [GLY]/[Pt] = 177).

TABLE 2

Product Distribution[a] at Maximum Glyoxylic Acid Yield and Initial Rate of Formation (38°C, pH 7.7, [GLY] = 0.1 mol liter^{-1}, [GLY]/[M] = 177)

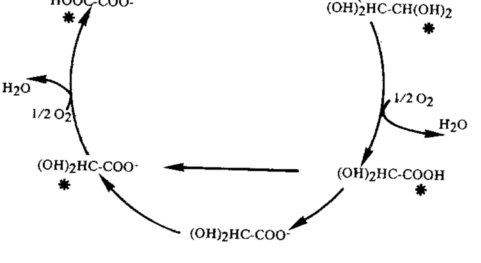
Catalyst	Glyoxal conversion (%)	Glyoxylic acid (%)	Oxalic acid (%)	Glycolic acid (%)	Formic acid (%)	Selectivity (%)	R^b
Pt/C	85.5	60	15.5	<2	<2	70	100
Ir/C	80	41	10	9	19	51	53
Pd/C	70	23	12.5	4	4	33	33
Rh/C	70	30.5	7	8	13.5	44	21
Ru/C	41	<1	<1	17	29	0	0

[a] In mol%; carbonates were not analyzed.

[b] Initial rate of glyoxylic acid formation (relative rates with respect to platinum, corrected for metal content).

at the expense of GLY. Although carbonate anions were not analyzed, the mass balance indicates by difference that 10% CO_2 should be formed by total oxidation on the Pt/C catalyst.

Since OX is produced mainly by the oxidation of GLY it can be concluded that glyoxal oxidation proceeds in two consecutive steps; Scheme 1 shows a tentative scheme for the catalytic cycle of glyoxal oxidation. Most probably one hydrated functional group of the glyoxal dihydrate molecule adsorbs on the metal surface and is oxidized via the dehydrogenation mechanism proposed earlier for alcohol and aldehyde hydrates (*24–26*). The adsorbed GLY molecule can then either desorb from the metal surface to be solvated in the liquid phase or remain adsorbed via the other functional group of the molecule and be oxidized into OX.



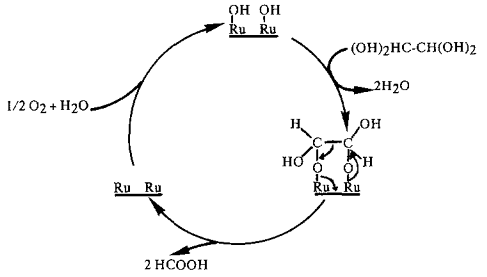
SCHEME 1

The desorption of GLY is faster than the oxidation of the second functional group since the GLY yield can be as high as 60% (Table 2). However, as the contact time increases, GLY readsorbs on the metal surface. This scheme does not specify the structure of the adsorbed species, but the initial adsorption of the glyoxal molecule must occur via only one functional group otherwise GLY would not be formed. The catalytic cycle is incomplete since it does not take into account the formation of carbon dioxide which can appear at the end of the cycle at the expense of OX or can be formed in a concurrent catalytic cycle where the glyoxal molecule would adsorb on the metal surface via the two functional groups. The glyoxal oxidation, unlike the glucose (*26–28*) or ethylene glycol oxidation (*29, 30*), goes to completion on platinum catalysts. Three is no surface poisoning by strongly chemisorbed oxygen probably because glyoxal and GLY are stronger reducing agents.

4. Oxidation on Ru, Rh, Pd, and Ir Catalysts

Table 2 gives the reaction data obtained on the different catalysts with the same ratio glyoxal/metal = 177.

Glyoxal oxidation carried out on the Ru/C catalyst was very sluggish and unselective.



SCHEME 2

Indeed after 26 h, the glyoxal conversion was only 41% and negligible amounts of GLY and OX were formed. Interestingly, the oxidation products were mainly formic acid (29%) and glycolic acid (17%). Oxidation at higher temperature increased the conversion but the product distribution was unchanged.

The formation of glycolic and formic acids could be explained by the presence of hydroxyl groups at the surface of ruthenium at pH 7.7 in water solution saturated with oxygen. Glycolic acid would be formed via the internal dismutation of the glyoxal molecule (Cannizzaro reaction) catalyzed by the basic hydroxyl groups. Formic acid could be produced by the catalytic cycle shown in Scheme 2, where the key step, namely the condensation of glyoxal dihydrate on two contiguous metal atoms covered by hydroxyl groups, has been suggested (*7*) to account for the formation of formic acid by oxidation of glyoxal on platinum electrodes at low potentials.

The Pd/C, Rh/C, and Ir/C catalysts have activities and selectivities intermediate between those of platinum and ruthenium and they also give intermediate amounts of glycolic and formic acids (Table 2). Interestingly, the initial rates of GLY formation increase in the same series (0 = Ru < Rh < Pd < Ir < Pt) as that of the redox potentials of these elements. The most easily oxidized metal, ruthenium, is covered by oxygen or hydroxyl groups so that the dehydrogenation mechanism leading to GLY does not occur. As the redox potential increases, the probability for the dehydrogenation mechanism increases.

It is interesting to compare these results with those obtained recently by van Dam *et al.* (*31*) in the autoredox reaction of formaldehyde to methanol and formate and in the methanol oxidation to formate on platinum-group metals. In the former reaction, the rate follows the series Ru $\gg$ Ir > Rh > Pd = Pt, which is the same as that observed in the autoredox reaction of glyoxal to glycolic acid (Table 2). Moreover, in methanol oxidation the sequence of metal activities is similar to that found in the oxidation of glyoxal to glyoxylic acid (Table 2) and the same interpretation was given, namely that the higher the work function the higher the stability toward oxygen poisoning.

CONCLUSION

This first attempt to oxidize glyoxal to glyoxylic acid with air near room temperature is encouraging. From a research and development standpoint, the prospect of producing this valuable synthon using trivial oxidation with air is very attractive. From an academic point of view, this study contributes to the knowledge on a much neglected domain of metal catalysis. The most interesting result is that platinum is capable of oxidizing glyoxal in two consecutive steps, yielding first glyoxylic acid and then oxalic acid. These successive oxidations imply a mechanism whereby glyoxal dihydrate molecules present in water solution are adsorbed end-on via one of the functional groups and are dehydrogenated into glyoxylic acid. The monoacid is then solvated at least transiently; it can either roll over and readsorb immediately to be transformed into oxalic acid by dehydrogenation of the second aldehyde hydrate or diffuse away from the metal surface. However, ultimately glyoxylic acid readsorbs and is oxidized. Other Group VIII metals are less active and also less selective than platinum, giving substantial amounts of glycolic and formic acids. We suggest that the formation of these products and the small activity of these catalysts, especially of ruthenium, is due to the presence of oxygen or hydroxyl groups covering the surface; the higher the oxidizability of the metal, the lower the initial rate of glyoxylic acid formation.

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