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The roles of chloride ions in the direct formation of H_2O_2 from H_2 and O_2 over a Pd/SiO_2 catalyst in a H_2SO_4/ethanol system

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Abstract

Hydrogen peroxide was produced directly from H_2 and O_2 over a Pd/SiO_2 catalyst in a slurry of ethanol that had been acidified with H_2SO_4. All reactions were carried out at atmospheric pressure and at 10 °C. The effects of chloride ions on the reactions involving the formation of H_2O_2, as well as the formation of water via the combustion of H_2 and the reduction or decomposition of H_2O_2, were investigated by adding small amounts of HCl to the system. In the absence of chloride ions, the net rate of H_2O_2 formation was very small, because the combustion reaction was dominant. At a Cl^- concentration of 4×10^{-4} M, the formation of H_2O_2 proceeded at a reasonable rate, with a selectivity of ca. 45% based on H_2 conversion. During the early stages of the reaction, hydrogen was consumed both in the formation of H_2O_2 and in the combustion reaction, but as more peroxide was formed, the reduction of H_2O_2 became a significant reaction. The positive effect of Cl^- on the surface Pd appears to result from the inhibition of O–O bond breaking in both dioxygen and hydrogen peroxide. The former effect limits the combustion reaction, and the latter limits the decomposition and reduction reactions. Chloride ions also inhibit the dissolution of palladium in H_2SO_4; in the presence of small amounts of Cl^-, the loss of Pd was generally <20% of the total amount in the catalyst.

Keywords: Hydrogen peroxide; Palladium/silica catalyst; Chloride promotion

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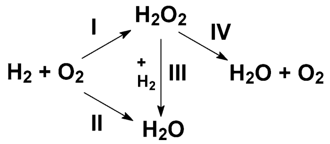
1. Introduction

Hydrogen peroxide is currently produced by the Riedl–Pfleiderer process, which involves the sequential hydrogenation and oxidation of an alkyl anthraquinone [1]. The direct synthesis of hydrogen peroxide from H_2 and O_2 over supported palladium, however, has attracted recent attention because the direct process may yield fewer side products and may be less expensive. The early work of Pospelova et al. [2,3] demonstrated that an inorganic acid, such as HCN or HCl, was essential for achieving large yields of peroxide in the direct synthesis. More recent studies have focused on the positive effects of chloride and bromide ions [4–12], but because of the complexity of the reaction network, the specific roles of these halide ions have not been completely elucidated. The effects of adding these ions, either directly to the reaction slurry or indirectly through the catalyst [10], is to increase the *net* rate of H_2O_2 formation and the selectivity for the conversion of H_2 to H_2O_2.

The four reactions that should be considered are given in Scheme 1. Only reaction I results in the formation of H_2O_2; the other three reactions result in the formation of H_2O and thus are undesirable. Pospelova et al. [2] suggested that Cl^- slows down the decomposition of H_2O_2, whereas, Hutchings et al. [9] concluded that Br^- suppresses the hydrogen combustion (reaction II). Burch and Ellis [7] pointed out that halide ions may inhibit the dissociation of dioxygen either by blocking adjacent sites on the palladium surface or by modifying the electron density on the metal surface, and thus affect its reactivity. We previously demonstrated that relatively large amounts of Br^-



Scheme 1. Reactions involved in the direct formation of H_2O_2.

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(e.g., 1×10^{-3} M) resulted in a decrease in the net formation rate, presumably by extensively blocking the surface palladium and decreasing the rate of reaction I [12]. The effect of Cl^- is less, even at much larger concentrations [12].

The research described here provides more detailed information on the relative importance of reactions II–IV in limiting the net rate of H_2O_2 formation, the selectivity, and the maximum concentration of H_2O_2 that can be achieved for a range of Cl^- concentrations while maintaining essentially the same proton concentration. Ethanol was chosen as the solvent because the solubilities of H_2 and O_2 in this liquid phase were larger than in water.

2. Experimental

The catalyst used in this study was 5 wt% Pd/SiO_2 prepared by the incipient wetness method using aqueous $PdCl_4^{2-}$ and Cab-O-Sil M5 silica, which is a fumed silica with a surface area of about 200 $m^2\,g^{-1}$. The $PdCl_4^{2-}$ was formed by dissolving $PdCl_2$ in concentrated HCl, followed by dilution with distilled water. After the solution was added to the silica, the material was dried in air at 120 °C overnight, heated in flowing O_2/He (20/40 $mL\,min^{-1}$) at 400 °C for 3 h, cooled in flowing He to 300 °C, and finally reduced in flowing H_2/He (20/40 $mL\,min^{-1}$) for 2 h. Previous XPS results confirmed that the supported palladium was present as Pd(0) both after the reduction step and after the catalytic reaction in ethanol [12].

The reactions were typically carried out at atmospheric pressure and at 10 °C in glass reactors described previously [8]. One of these reactors was open to the atmosphere, whereas the other reactor was closed and had a vent that exited to a gas chromatograph (HP 5890 with a 5A molecular sieve column operating at 30 °C), so the composition of the gas could be analyzed for H_2 and O_2. To improve the accuracy of the analysis, a mixture of H_2/N_2 containing 10% N_2 was used. The gases were introduced at a total flow rate of 50 $mL\,min^{-1}$ via a glass frit (Ace, 4–8 µm) at the bottom of the reactor.

The liquid phase consisted of 50 or 60 mL of ethanol acidified with sulfuric acid to 0.12 M. The lesser amount of ethanol was used for the decomposition reactions; the larger amount, for the formation reactions. The desired chloride concentration was attained by adding appropriate amounts of aqueous HCl. The addition of both acids introduced small amounts of water to the system.

The O_2/H_2 ratio of 4:1 used in these experiments is in the explosive regime; therefore, appropriate precautions should be taken. In particular, the dry catalyst *should not* be added to O_2/H_2 gas mixture. Hence, the protocol for adding the catalyst was as follows: (a) The ethanol was exposed to the O_2/H_2 gas mixture via the frit for 30 min; (b) 5 mL of the liquid phase was taken out of the reactor, and a slurry was made with 42 or 50 mg of catalyst; and (c) this slurry was added to the remaining solution in the reactor. The amount of catalyst depended on the amount of ethanol; that is, 42 mg of catalyst was used with 50 mL of ethanol, and 50 mg of catalyst was used with 60 mL of ethanol.

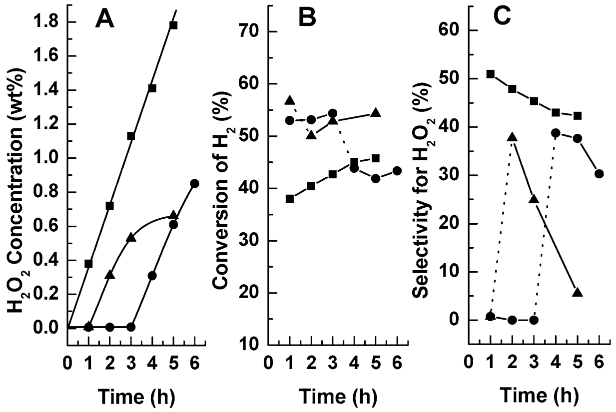

Fig. 1. Direct formation of H_2O_2 in H_2SO_4/ethanol system with (■) 4×10^{-4} M Cl^- introduced initially, (●) no Cl^- present initially and 4×10^{-4} M Cl^- introduced after 3 h, and (▲) no Cl^- present initially and 2×10^{-5} M Cl^- introduced after 1 h: (A) H_2O_2 concentration, (B) conversion of H_2, and (C) selectivity for H_2O_2.

At appropriate times after the reaction had been initiated by the addition of catalyst, the gas phase was analyzed and the conversion of H_2 determined. In addition, an aliquot of the liquid phase (ca. 0.2 g) was removed and analyzed for H_2O_2 using a colorimetric method with a $TiOSO_4/H_2SO_4$ reagent [13]. From the net rate of H_2O_2 formation and the rate of H_2 conversion, the selectivity for H_2O_2 could be determined using the following equation:

$$S_{H_2O_2} = \frac{\text{Rate of } H_2O_2 \text{ formation (mol/min)}}{\text{Rate of } H_2 \text{ conversion (mol/min)}} \times 100. \tag{1}$$

3. Results

3.1. Formation of H_2O_2

The formation of H_2O_2 as a function of time at two different chloride concentrations is depicted in Fig. 1A. At a Cl^- concentration of 4×10^{-4} M, the *net* formation of H_2O_2 increased in a nearly linear manner for a period of 5 h to a level of 1.78 wt%. This corresponds to a rate of formation of 34 $mmol_{H_2O_2}\,g_{Pd}^{-1}\,min^{-1}$ (102 $mol_{H_2O_2}\,kg_{cat}^{-1}\,h^{-1}$). In a separate experiment, the reactor was thoroughly cleansed of any residual Cl^-, and the reaction was carried out in the usual manner for 3 h. In the absence of added Cl^- there was almost no net formation of H_2O_2 (<0.008 wt%), but when Cl^- was added to a level of 4×10^{-4} M, the net rate of H_2O_2 formation was about the same as that observed in the initial experiment. In a previous paper [14], we stated that even in the absence of Cl^-, H_2O_2 was produced with the H_2SO_4/ethanol system; however, it now appears that the reactor had not been thoroughly cleaned, and the residual Cl^- was sufficient to promote the net reaction. Only very small amounts of Cl^- are necessary to initiate the net formation of H_2O_2, as illustrated by the experiment in which the slurry was made only 2×10^{-5} M in Cl^-. In this case the net H_2O_2 formation rate was initially about the same as that observed with the much larger chloride ion concentration, but after 2 h at this smaller Cl^- concentration, the rate decreased markedly.

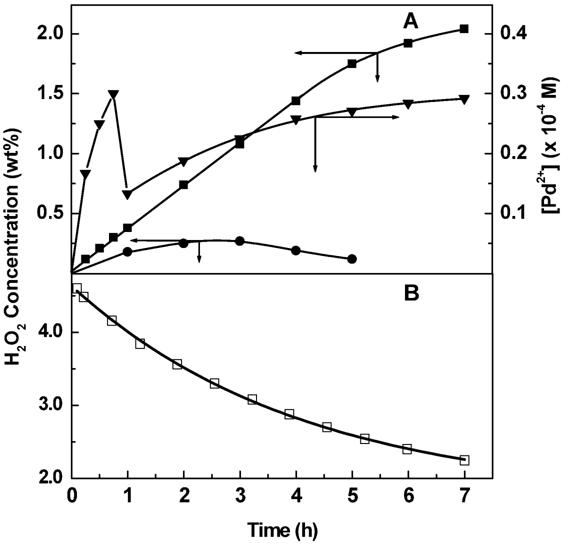

Fig. 2. (A) Net formation of H_2O_2 at (■) 4×10^{-4} M Cl^- and (●) 4×10^{-6} M Cl^-; (▼) concentration of Pd^{2+} in solution as a function of time for 4×10^{-4} M Cl^-; (B) Net decrease in the concentration of H_2O_2 in the presence of H_2 and O_2 ($O_2/H_2 = 4$) with 4×10^{-4} M Cl^-. The initial concentration of H_2O_2 in (B) was 4.6 wt%.

It is also instructive to consider the effect of chloride concentration on the H_2 conversion level (Fig. 1B). Surprisingly, in the absence of Cl^-, when there was almost no net formation of H_2O_2, the conversion of H_2 was the greatest, about 55%. When Cl^- was added to the system, H_2 conversion decreased proportionally to the amount of Cl^- introduced. In the presence of Cl^-, H_2 conversion generally increased with time, which had a negative effect on selectivity, as shown in Fig. 1C. For example, at a Cl^- level of 4×10^{-4} M, the selectivity decreased from 50 to 42% in 5 h. At a Cl^- level of 2×10^{-5} M, the decrease in selectivity was much larger. Obviously, the selectivity was nearly zero in the absence of added Cl^-.

The longer-term net formation of H_2O_2 at two different Cl^- concentrations is shown in Fig. 2A. Even at a Cl^- concentration of 4×10^{-4} M, the net rate began to decrease after 5 h, and at a concentration of 4×10^{-6} M, the rate decreased after 1 h, and the H_2O_2 concentration reached a maximum at ca. 3 h. At 4×10^{-3} M Cl^- (results not shown), the net rate of H_2O_2 formation was somewhat greater than at 4×10^{-4} M Cl^- for the first 3 h, but at longer reaction times, the rate became smaller. After 5 h, the H_2O_2 concentration was 2.0 wt%.

In an attempt to understand the origin of this loss in activity with time, the loss Pd from the catalyst and the amount of Pd^{2+} in solution were determined for the system containing 4×10^{-4} M Cl^-. The latter is also shown in Fig. 2A. The concentration of Pd^{2+} in solution was determined using the method of Onishi [15]. The amount of palladium remaining on the surface was determined after different reaction times by first centrifuging the slurry, thereby removing the catalyst and any other solid material from the slurry. Then an aqueous 0.6 M HCl solution was added to the solid residue. After allowing the new slurry to stand overnight in air, the liquid phase was analyzed for Pd^{2+}. The method was confirmed by analyzing a fresh Pd/SiO_2 catalyst. Assuming that all of this Pd dissolved, the molar equivalent would be 3.9×10^{-4} M. It was also shown that the relatively large particles of palladium black formed during the catalytic reaction were not oxidized to Pd^{2+} under these conditions. These larger unoxidized particles were observed only after the reaction had been carried out at the largest Cl^- concentration, namely 4×10^{-3} M.

Here it should be noted that the Pd^{2+} is in a dynamic state with palladium remaining on the catalyst and deposited on the frit, as well as any that may be present in the slurry as palladium black. Thus, the amount of Pd^{2+} in solution is expected to be somewhat less than the total amount lost from the catalyst. The results of Fig. 2A clearly indicate that the concentration of Pd^{2+} reached a maximum value of 0.30×10^{-4} M after about 45 min, and then decreased abruptly. This maximum was $<10\%$ of the total amount of Pd in the system. After the abrupt decrease, the concentration increased slowly to 0.29×10^{-4} M after 420 min. During the early stage of the reaction, the dissolved Pd^{2+} apparently was in a metastable state, and after about 45 min into the reaction, more than half of it was reduced to a form of Pd^0 that is not readily reoxidized. Thereafter, part of this palladium was slowly oxidized to Pd^{2+}. It is important to note that during the first 45 min, while the Pd^{2+} concentration was first increasing and then decreasing, the net rate of H_2O_2 formation remained constant.

In a set of two experiments carried out for 4 h and 7 h under the same conditions, it was determined that the amount of Pd remaining on the surface was the equivalent of 3.3×10^{-4} and 2.9×10^{-4} M, respectively. Thus, the amount of Pd lost from the surface was about 20%, and at least half of this loss occurred relatively early in the reaction. In fact, only 10% of the loss occurred between the fourth and seventh hours of the reaction. Thus, it seems unlikely that loss of palladium from the surface can account for the decrease in the net rate of H_2O_2 formation after 5 h (Fig. 2A). Moreover, the marked changes in the Pd^{2+} concentration after 45 min of reaction were not reflected in the H_2O_2 formation rate.

As a blank experiment, the loss of palladium was followed in the usual H_2SO_4/ethanol system but with no Cl^- present. Unexpectedly, the Pd^{2+} concentration reached a maximum value of 0.88×10^{-4} M after 50 min, which is considerably greater than that observed when the slurry was 4×10^{-4} M in Cl^-. But after 370 min of reaction, the Pd^{2+} concentration in the absence of chloride ions had decreased to only 0.05×10^{-4} M. After 7 h under reaction conditions, the Pd remaining on the SiO_2 was the equivalent of 2.6×10^{-4} M. Therefore, one long-term role of the chloride is to reduce the loss of Pd in the sulfuric acid solution somewhat. This inhibition was also observed for other chloride concentrations.

3.2. *Reduction and decomposition of H_2O_2*

Because the loss of palladium cannot fully account for the decrease in the net rate of H_2O_2 formation after ca. 5 h, other explanations must be sought. One explanation is that a steady state is reached between the true rate of H_2O_2 formation and its rate of reduction and/or decomposition. Evidence for such a steady state is found in the *net* rate of H_2O_2 reduction/decomposition depicted in Fig. 2B. This experiment was carried out in the standard system with $O_2/H_2 = 4$ and a Cl^- concentration of 4×10^{-4} M; hydrogen peroxide was added to the initial slurry to attain a concentration of 4.6 wt%. Over 7 h, the concentration of H_2O_2 decreased to 2.2 wt%, comparable to the 2.0 wt% formed in the conventional system to which no H_2O_2 was added (Fig. 2A). A similar experiment was carried out at a Cl^- concentration of 2×10^{-5} M. Hydrogen peroxide was added to achieve an initial concentration of 1.7 wt%. In the presence of O_2 and H_2, the H_2O_2 concentration decreased in a nearly first-order manner to 0.4 wt% over 4 h, in reasonable agreement with the steady-state concentration of 0.6 wt% shown in Fig. 1A. Thus, a nearly common steady-state level of H_2O_2 was achieved by both the net loss and the net formation reactions.

To further explore the *net* decomposition rate of H_2O_2 at different chloride ion concentrations, the reaction was allowed to proceed for 1 h with $O_2/H_2 = 4$ at a particular Cl^- concentration, and then ca. 1.7 wt% H_2O_2 was added to the system. The concentration of H_2O_2 was followed as a function of time; the results are given in Fig. 3. In the absence of any added Cl^-, the net loss of H_2O_2 was rapid (Fig. 3A), and after 90 min, the concentration approached the detection limit. The results are shown as a first-order plot in Fig. 3B for this case and for several Cl^- concentrations. Clearly, the Cl^- ion concentration had a significant effect on the net loss of H_2O_2, with the most marked change between 4×10^{-6} and 2×10^{-5} M. At 4×10^{-3} M Cl^-, there was a net increase in H_2O_2 concentration. Although the net change in H_2O_2 concentration was not strictly first order, the results are given as first-order rate constants in Table 1 for purposes of comparison. Over the range of Cl^- investigated, the rate constants differed by more than two orders of magnitude.

The decrease in H_2O_2 concentration in the absence of added Cl^- was determined with different gasses passing through the reactor; the results are shown in Fig. 4. The first-order rate constants are also given in Table 1. The largest rate constant was observed with the N_2/H_2 mixture, which suggests the role of H_2 in the loss of H_2O_2; however, as shown below, the reduction reaction is not the dominant pathway in the absence of Cl^-. Oxygen, in contrast, had a stabilizing effect on the H_2O_2.

Although these experiments show the effects of Cl^- ion concentration and gas composition on the stability of H_2O_2, they do not provide information on the more fundamental question concerning the relative importance of reduction and decomposition reactions. To explore these reactions, we took advantage of the fact that the reduction reaction consumes H_2 while the decomposition reaction releases O_2. Using the closed reactor, a set of experiments was conducted in which a N_2/H_2 (4:1) mixture was passed through the standard H_2SO_4/ethanol solution that contained different concentrations of chloride ions. At a specific time, H_2O_2 was introduced to a level of 1.7 wt%, after which the H_2 and O_2 concentrations were determined as functions of time. At a Cl^- concentration of 4×10^{-4} M, the conversion of H_2 was nearly 50% during much of the decomposition reaction (Fig. 5), and O_2 was detected at only the background level. Hence, only the reduction reaction occurred at this chlo-

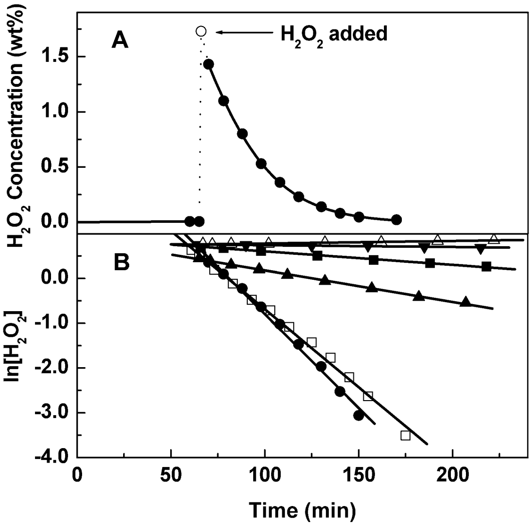

Fig. 3. Decomposition of H_2O_2 under $O_2/H_2 = 4$; 1.7 wt% H_2O_2 was added 60 min after the reaction had begun: (A) H_2O_2 concentration with respect to time in the absence of Cl^- and (B) $\ln[H_2O_2]$ versus time in the presence of (●) 0 M Cl^-, (□) 4×10^{-6} M Cl^-, (▲) 2×10^{-5} M Cl^-, (■) 4×10^{-5} M Cl^-, (▼) 4×10^{-4} M Cl^- and (△) 4×10^{-3} M Cl^-.

Table 1
Rate constants for the decomposition of H_2O_2

$[Cl^-]$ (M)	Gases composition	Decomposition rate constants (min^{-1})[a]
0	N_2/H_2 (4/1)	6.5×10^{-2}
0	O_2/H_2 (4/1)	4.2×10^{-2}
0	He only	2.8×10^{-2}
0	O_2 only	2.1×10^{-2}
4×10^{-4}	N_2/H_2 (4/1)	8.6×10^{-3}
4×10^{-6}	O_2/H_2 (4/1)	3.5×10^{-2}
2×10^{-5}	O_2/H_2 (4/1)	7.0×10^{-3}
4×10^{-5}	O_2/H_2 (4/1)	3.0×10^{-3}
4×10^{-4}	O_2/H_2 (4/1)	4.1×10^{-4}
4×10^{-3}	O_2/H_2 (4/1)	-5.6×10^{-4}

[a] When O_2 and H_2 are present these are rate constants for the net loss of H_2O_2.

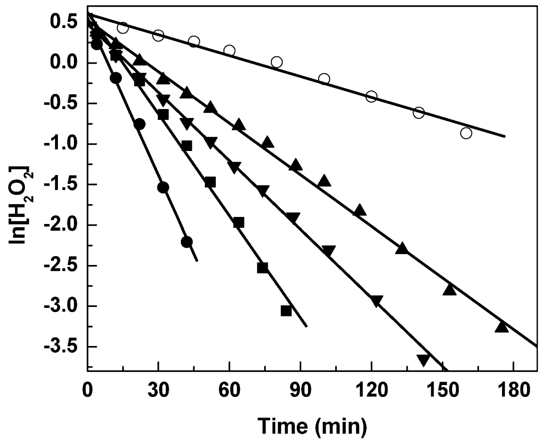

Fig. 4. Decomposition of H_2O_2 in the absence of Cl^- ions with different gases: (●) $N_2/H_2 = 4$, (■) $O_2/H_2 = 4$, (▼) He and (▲) O_2, as well as (○) $N_2/H_2 = 4$ in the presence of 4×10^{-4} M Cl^-.

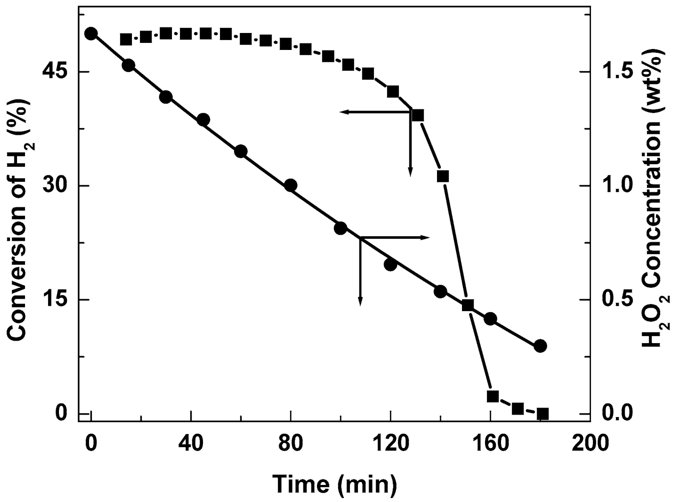

Fig. 5. The conversion of H_2 (■) and the concentration of H_2O_2 (●) as a function of time in flowing $N_2/H_2 = 4$. The Cl^- concentration was 4×10^{-4} M.

ride level. In a parallel reaction, the decrease in the amount of H_2O_2 was followed; these results are also shown in Fig. 5. For these conditions, the loss of H_2O_2 was nearly zero order until almost all of the peroxide had been reduced; nevertheless, for comparison purposes, the results are plotted in a first-order reaction format in Fig. 4, and the rate constant is given in Table 1. Near the end of the reaction, H_2 conversion decreased because the residual amount of H_2O_2 became small. Because H_2 conversion remained essentially constant throughout most of the reaction, even as the H_2O_2 concentration decreased significantly, hydrogen transport may have been a limiting factor.

With smaller chloride ion concentrations, the decomposition reaction became significant, as indicated by the presence of O_2 as a product. From the amounts of O_2 and H_2 in the effluent from the reactor and the stoichiometry of the decomposition and reduction reactions, a ratio of decomposition to reduction (D/R) can be calculated. Fig. 6 depicts the conversion of H_2 and the D/R ratio for systems containing no Cl^- and 1×10^{-5} M Cl^-. With 1×10^{-5} M Cl^-, H_2 conversion was 42% during most of the reaction, which means that the extent of the hydrogen consumption decreased only slightly with a 40-fold decrease in the Cl^- concentration. But the D/R ratio increased from 0 with 1×10^{-4} M Cl^- to ca. 2.4 with 1×10^{-5} M Cl^-. The latter D/R ratio was attained soon after the introduction of H_2O_2 to the system, but as the H_2O_2 was decomposed/reduced, the D/R ratio decreased in a continuous manner. A D/R ratio of ca. 2 suggests that at the intermediate Cl^- concentration, H_2O_2 is formed under normal reaction conditions (i.e., $H_2 + O_2$), but it is decomposed according to reaction IV.

When no chloride was added to the system, the initial D/R ratio was 14 (Fig. 6B), which indicates that decomposition mainly occurred. Again, as the H_2O_2 was consumed, the D/R ratio decreased. As shown in Fig. 6A, H_2 conversion first increased to a maximum of 35% and then decreased. The smaller initial conversion of H_2 may result from the formation of O_2 bubbles on the surface, which inhibits the diffusion of H_2 to the Pd particles. The decrease resulted from the nearly complete depletion of H_2O_2.

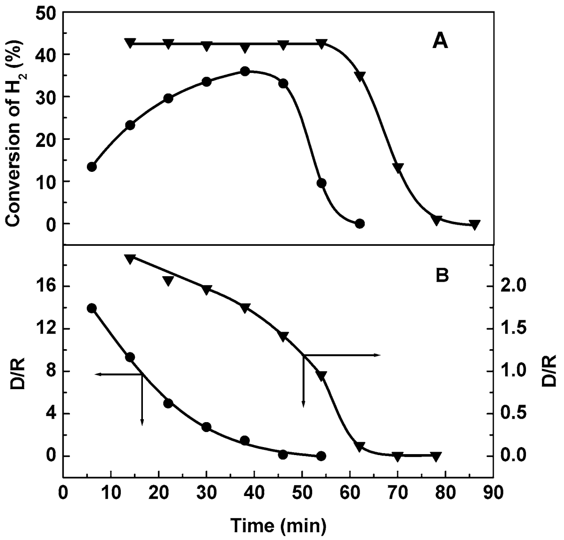

Fig. 6. (A) The conversion of H_2 and (B) the ratio of decomposition-to-reduction (D/R) as a function of time in flowing $N_2/H_2 = 4$: (●) in the absence of Cl^- and (▼) in 1×10^{-5} M Cl^-.

4. Discussion

4.1. Analysis of the kinetic data

Interesting conclusions concerning the relative rates of the reactions described in Scheme 1 can be deduced from the kinetic data. We first consider the system with 4×10^{-4} M Cl^-. The experiments described above, which were carried out in the absence of added O_2, confirmed that the decomposition of H_2O_2 (reaction IV) is minimal at this chloride concentration and that most of the H_2O_2 is lost via reduction (reaction III). Under normal reaction conditions, however, the extent to which H_2 is consumed by reactions I and II has not been determined, but one can qualitatively evaluate the significance of these reactions by considering the selectivity for H_2O_2 formation and the extent to which reaction III might occur. During the early stages of the reaction, the H_2O_2 concentration would be small; therefore, the loss of peroxide by reduction would approach zero. The observed selectivity of about 50% suggests that about half of the H_2 reacts to form H_2O_2 and half reacts to form H_2O. From Fig. 1A, one can determine that the *net* rate of H_2O_2 formation is 8.4×10^{-5} mol min^{-1}, but this is also the *true* rate of peroxide formation, because secondary reactions are negligible. The rate of H_2 consumption would be twice this amount; that is, 16.8×10^{-5} mol min^{-1}. From the results of Fig. 5, it is evident that the reduction of H_2O_2 also can be significant, but again, its contribution to the overall reaction depends on the amount of peroxide that has accumulated. In the absence of O_2, the rate of reduction, based on H_2 consumption, was 1.0×10^{-4} mol min^{-1} for H_2O_2 concentrations > ca. 0.8 wt%, but during the actual formation of H_2O_2, the rate of reduction would be much less than this, because reactions I and II would also compete for the available H_2. The purpose of this analysis is to show that the reduction of the peroxide will become significant only at the higher H_2O_2 concentrations. The decrease in the net rate of formation after 4 h (Fig. 2A) probably results from the contribution of this reduction reaction.

In the absence of added Cl^- ions, the contribution of reaction II appears to be quite different. The net formation of H_2O_2 is very small (Fig. 1A), which conceivably could result from the very rapid decomposition or reduction of H_2O_2, however the rates of either or both of these reactions would have to be much greater than those determined from the results of Fig. 4. The H_2 conversion decreased by only a modest amount when Cl^- was added to the system (Fig. 1B), suggesting that the reduction reaction was not responsible for the small net formation of H_2O_2. Moreover, the rate of H_2 conversion in the absence of chloride ions was ca. 2.3×10^{-4} mol min^{-1} (Fig. 5), which is only 28% more than the true formation rate and clearly not sufficient to account for the fact that there was almost no net formation of H_2O_2. As shown in Fig. 6, the decomposition reaction became less significant as the H_2O_2 concentration approached zero. It seems reasonable, therefore, that the inability to form H_2O_2 in the absence of chloride ions is a result of the rapid combustion of H_2 (reaction II), which is in contrast to the case in which the Cl^- concentration was 4×10^{-4} M.

At intermediate Cl^- concentrations, reactions II, III, and IV all probably contribute to the inefficient utilization of H_2. For low concentrations of H_2O_2, $D/R < 1$; however, at higher concentrations of peroxide, decomposition is relatively more important (Fig. 6). But again the decomposition/reduction reactions do not become significant in the net synthesis reaction until an appreciable concentration of H_2O_2 is attained.

4.2. *Interpretation of the results*

It is obvious from the preceding sections that chloride ions influence the side reactions and sequential reactions that limit the net rate of H_2O_2 formation, the selectivity for H_2O_2, and the maximum concentration that can be attained in the semibatch system. In previous work attention was given to the role of Cl^- (or Br^-) in blocking sites for the dissociation of O_2, thereby inhibiting the combustion reaction [7,9]. With the new information concerning the importance of the different possible reactions, it now seems that Cl^- may play several roles, depending on the concentration of halide and the amount of peroxide in the system. Before considering the mechanism by which Cl^- operates, one should note the concentrations of the Pd, particularly the surface concentration, and the concentration of Cl^- ions. Based on the size of the Pd particles reported in an earlier study [12], the Pd dispersion has been estimated to be about 20%; that is, about 20% of the Pd atoms are on the surface. The molar equivalent of surface Pd in our system would be about 8×10^{-5} M. The results of Fig. 1A demonstrate, however, that even 2×10^{-5} M Cl^- leads to the formation of a significant amount of H_2O_2, and a slurry that is 4×10^{-6} M in Cl^- also exhibits activity for the net formation of H_2O_2 (Fig. 2). Moreover, it is unlikely that all of this Cl^- is adsorbed on the Pd; some of it is complexed as $PdCl_4{}^{2-}$. This comparison of Pd and Cl^- concentrations suggests that either large ensembles of Pd atoms are required for the combustion reaction, and a single chloride ion can affect such an ensemble, or there are long-range electronic effects that modify the catalytic activity of the palladium.

Whether by site blocking or through an electronic effect, the major role of Cl^- appears to be that of limiting the combustion reaction (reaction II), probably by keeping the O–O bond intact as O_2 is adsorbed. If the combustion reaction can be limited, H_2O_2 will be formed, but it is subject to both decomposition and reduction. The decomposition reaction also involves the breaking of an O–O bond, and the effect of Cl^- on this reaction may be similar to its effect on the combustion reaction. Previously, a mechanism for the dissociation of H_2O_2 over gold via $OH^{\bullet}$ radicals was proposed [16]. The mechanism for the reduction of H_2O_2 is not known, but also may involve the formation of $OH^{\bullet}$ radicals, followed by the reaction of these radicals with surface H atoms. Thus, the major positive role of Cl^- appears to be the inhibition of O–O bond breaking in both O_2 and H_2O_2.

5. Conclusion

Chloride ions, even in small concentrations, have a strong positive effect on the net formation of hydrogen peroxide. Their main role is inhibiting the combustion of hydrogen; however, they also limit the reduction and decomposition of H_2O_2. In the absence of Cl^- ions, the dominant reaction is the combustion of H_2, but on addition of Cl^- ions, the direct formation of H_2O_2 becomes more favorable. Moreover, as chloride is added to the system, the reduction of H_2O_2 becomes favored over the decomposition of the peroxide. The fundamental role of Cl^- appears to be the inhibition of O–O bond breaking during the adsorption of dioxygen and hydrogen peroxide. This may be achieved by blocking Pd ensembles on the surface or by electronic effects. Chloride ions have a secondary role in controlling the dissolution of the supported palladium as Pd^{2+} (or $PdCl_4{}^{2-}$) in the liquid phase.

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