Notes

The Easy Catalytic Reduction of $HClO_4$, HNO_3, and H_5IO_6 by CO in the Presence of $[Pd_3(O_2CMe)_6]$ †

Renato Ugo* and Anna Chiesa
Dipartimento di Chimica Inorganica e Metallorganica dell'Università, Via Venezian 21, 20133 Milano, Italy
Anatoli Yatsimirski
Chemical Department, Moscow State University, 117234 Moscow, U.S.S.R.

The reduction of $HClO_4$ to HCl by CO, catalysed in acetic acid by $[Pd_3(O_2CMe)_6]$, is reported together with the parallel formation of either $[\{Pd(CO)Cl\}_n]$ or β-$PdCl_2$ according to the reaction conditions. Under similar conditions HNO_3 is reduced first to NO_2 and then to NO; the known compound $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$ is the final product. With H_5IO_6 only insoluble PdI_2 is obtained under each reaction condition, corresponding to an easy reduction by CO of H_5IO_6.

The oxidative carbonylation of unsaturated hydrocarbons catalysed by palladium salts is of interest at present.[1] In particular with aromatic substrates the palladium-mediated synthesis of aromatic acids or their derivatives has been described *via* aryl-mercury(II)[2a] or –thallium(III)[2b] derivatives as active arylation intermediates. The direct oxidative carbonylation of simple aromatic hydrocarbons by $[Pd_3(O_2CMe)_6]$ occurs with low yields and slow reaction rates, the competiting reaction being the reduction of palladium salts to metallic palladium.[3]

It is known that the addition of strong acids, such as $HClO_4$, facilitates the oxidative coupling of aromatic hydrocarbons catalysed by palladium(II) salts;[4] as a consequence we investigated the effect of the addition of strong acids, such as $HClO_4$. Under carbonylation conditions (*e.g.*, oxidation of benzene under a CO atmosphere with palladium acetate, working in acetic acid solution) we observed that the addition of some $HClO_4$ (concentration higher than 0.05 mol dm^{-3}) stopped completely both the reduction of the palladium salt to metallic palladium and the parallel oxidative carbonylation of benzene to benzoic acid. Under these conditions a stable solution was obtained from which the known compound $[\{Pd(CO)Cl\}_n]$[5] could be isolated.

It is known from the work of Moiseev *et al.*[6] that by addition of 1—3 atm of CO to a solution of $[Pd_3(O_2CMe)_6]$ in dry acetic acid, the cluster $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$ separates slowly; by addition of small amounts of an acid like $HClO_4$ (0.05 mol dm^{-3}) fast reduction to metallic palladium occurs even in the complete absence of water. Obviously we observed a quite different behaviour and this fact stimulated a more extensive investigation of the reaction of different strong oxyacids, in particular $HClO_4$, HNO_3, and H_5IO_6, with carbon monoxide in the presence of $[Pd_3(O_2CMe)_6]$.

Results and Discussion

Effect of the Addition of $HClO_4$.—When concentrated $HClO_4$ is added, under 3 atm of carbon monoxide, to a 0.05 mol dm^{-3} solution of $[Pd_3(O_2CMe)_6]$ in acetic acid (containing acetic anhydride in 10% excess with respect to the water added with concentrated $HClO_4$) metallic palladium does not separate, but a stable yellow solution is obtained together with a relevant oxidation of CO to CO_2.

When the $HClO_4$ concentration is between 0.15 and 0.25 mol dm^{-3}, the only compound which separates after 2 h is the yellowish form of the known polymeric carbonyl $[\{Pd(CO)Cl\}_n]$;[5] the yields {based on $[Pd_3(O_2CMe)_6]$} are between 85 and 55%, since they decrease with increasing concentration of $HClO_4$.

When the mother-liquor is left standing in air, however, a black material slowly separates; this product has i.r. absorption bands (in KBr pellets) at 1 980s and 1 940(sh) cm^{-1}, quite similar to those [1 980s and 1 920(sh) cm^{-1}] typical of $[\{Pd(CO)Cl\}_n]$. In addition it analyses quite close to Pd(CO)Cl, but always contains some $MeCO_2H$ and $HClO_4$ (weak i.r. bands at *ca.* 1 700 cm^{-1} for $MeCO_2H$ and a broad band around 1 280 cm^{-1} for $HClO_4$). When a suspension of this black material, in the same mother-liquor, is kept again under 3 atm of CO, it slowly converts into the yellowish form of $[\{Pd(CO)Cl\}_n]$. The overall reaction can be represented by equation (1).

$$\tfrac{2}{3}[Pd_3(O_2CMe)_6] + 2\,HClO_4 + 11\,CO \longrightarrow \tfrac{2}{n}[\{Pd(CO)Cl\}_n] + 9\,CO_2 + 2MeCO_2H + (MeCO)_2O \quad (1)$$

Increasing the concentration of $HClO_4$ gave $[\{Pd(CO)Cl\}_n]$ contaminated with another palladium material, but containing more chlorine. When the $HClO_4$ concentration is higher than 0.45 mol dm^{-3}, only a brown product, which analyses as $PdCl_2$, separates. This compound does not show any i.r. band in the region 4 000—600 cm^{-1} and is soluble in aromatic solvents. It was found to be the β-form of $PdCl_2$.[7] Yields are only *ca.* 50% when referred to the initial palladium acetate. From the mother-liquor, on standing, an amount of the black material described above separates. It is unlikely that reoxidation of metallic palladium, which slowly separates, occurs since it is reported that $HClO_4$ of similar concentration cannot reoxidize metallic palladium under rather similar conditions, corresponding to the reaction of coupling of aromatic hydrocarbons.[4]

With another strong, but non-oxidising acid such as HBF_4, only a fast reduction to metallic palladium occurs at any concentration of HBF_4. Thus it appears that under the above described conditions the easy reduction of rather diluted ClO_4^- to Cl^- occurs, according to reaction (2). This reaction is

$$ClO_4^- + 4\,CO \longrightarrow Cl^- + 4\,CO_2 \qquad (2)$$

homogeneously catalysed by palladium acetate. It is difficult at this stage to define what soluble form of palladium is the true

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† *Non-S.I. units employed:* atm = 101 325 N m^{-2}, eV ≈ 1.60 × 10^{-19} J.

catalyst, however we can propose that the addition of a strong protonic acid is a necessary condition to produce *in situ* a co-ordinatively unsaturated species of high electrophilic power[4] through a reaction like (3). It is likely that carbon monoxide

$$[Pd_3(O_2CMe)_6] + H^+ \rightleftharpoons [Pd_3(O_2CMe)_5]^+ + MeCO_2H \quad (3)$$

links to this co-ordinatively unsaturated species of palladium. In addition the presence of a positive charge and consequently the increased electrophilic character makes carbon monoxide more sensitive to any further nucleophilic attack.

When the concentration of $HClO_4$ is too low, the preferred nucleophilic attack is by $MeCO_2^-$ to form metallic palladium and acetic anhydride,[8] but at higher $HClO_4$ concentration the presence of some ClO_4^- favours its attack on co-ordinated and activated CO to form CO_2 and ClO_3^- respectively.

When the nucleophile is too poor or has non-oxidising properties such as BF_4^-, attack by $MeCO_2^-$ still prevails, and palladium separates. The basicity order of $HClO_4$, $HClO_3$, $HClO_2$, and HClO (pK_a of −10, −1, 2, and 7.2 respectively[9]) suggests a higher nucleophilic character for the intermediate oxygenated ions (*i.e.* ClO_3^-, ClO_2^-, and ClO^-) when compared to ClO_4^-, so that the reduction process stops only at the final level of chloride ion. Palladium chloride, formed *in situ*, can be subsequently reduced, if precipitation of β-$PdCl_2$ does not occur, to $[\{Pd(CO)Cl\}_n]$.[5]

It appears that Pd^{II} rather than Pd^{I} species are catalytically active in the reduction of ClO_4^-, since after conversion of all the palladium into $[\{Pd(CO)Cl\}_n]$ the absorption of carbon monoxide immediately stops, together with ClO_4^- reduction.

The proposed mechanism is supported also by the fact that the presence of strong acidity is a necessary requirement for the reduction of ClO_4^-. Addition of only $NaClO_4$ produces a slow separation of $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$.[6] This is another interesting observation since it is known that addition of a nucleophile like NaO_2CMe favours a fast reduction to metallic palladium with parallel formation of acetic anhydride.[8]

Effect of the Addition of HNO_3.—After addition at room temperature of rather small amounts (*ca.* 0.1 mol dm^{-3}) of HNO_3 to a 0.05 mol dm^{-3} solution of $[Pd_3(O_2CMe)_6]$ in $MeCO_2H$ (maintained under 2—3 atm of CO) the known cluster $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$[6] separates, in quantitative yields and after only 1 h. Reduction to metallic palladium is not observed. Working at higher concentrations of HNO_3 (0.15—0.3 mol dm^{-3}), reduction of HNO_3 first to NO_2 and later to NO is clearly observed. With similar HNO_3 concentrations and under several different reaction conditions a few palladium intermediates, which are under investigation, can be isolated, but the final product is $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$.

With this latter cluster the reduction of HNO_3 is completely inhibited. Differently from the ClO_4^- ion, the reduction of NO_3^- does not require strong acidity. In fact when HNO_3 is substituted with $LiNO_3$ the same intermediates and reaction products are observed the only difference being much lower reaction rates. Obviously this different behaviour must be ascribed to the higher nucleophilic character of NO_3^- when compared to ClO_4^-.

Effect of the Addition of H_5IO_6.—When H_5IO_6 is added at room temperature to a 0.05 mol dm^{-3} solution of $[Pd_3(O_2CMe)_6]$ in acetic acid (under 2—3 atm of CO) a quick separation of insoluble black PdI_2 occurs. The same reaction occurs at any concentration of H_5IO_6 (0.1—0.4 mol dm^{-3}).

Conclusions

We have shown that strong oxyacids such as $HClO_4$, which are usually added as a co-catalyst in some oxidation reactions of unsaturated hydrocarbons catalysed by palladium salts (in particular carboxylates),[4] can behave as an oxidant under mild conditions with regard to CO, producing *in situ* palladium complexes which are catalytically inactive. It is noteworthy that the palladium catalysis strongly increases the oxidative properties towards CO of acids such as $HClO_4$ or HNO_3, which are usually very weak oxidants when diluted. To our knowledge this report is the first example of an easy reduction of very dilute perchloric acid working under very mild conditions.

Experimental

Determination of Spectra.—I.r. spectra were recorded on a Perkin-Elmer 457 instrument as KBr pellets, mass spectra were recorded on a Varian Mat 112 mass spectrometer at 70 eV and 150 °C.

Reagents and Materials.—Palladium acetate was prepared according to Wilkinson and co-workers.[10] The reference compounds β-$PdCl_2$ and $[\{Pd(CO)Cl\}_n]$ were prepared by literature methods.[5,7] All chemicals and solvents were reagent grade and used as received.

Analysis.—Carbon and H analyses were carried out in the microanalytical laboratory of Milan University; Pd and Cl analyses were done either in this laboratory or at the F. Pascher Laboratory, Bonn.

Reduction of $HClO_4$.—Palladium acetate (200 mg) was dissolved in acetic acid (20 cm^3), containing $HClO_4$ (0.15 mol dm^{-3}) and enough acetic anhydride to react with the water added with concentrated $HClO_4$ (10% excess with respect to the stoicheiometric amount). By stirring, under 3 atm of CO and at room temperature, a yellowish precipitate, characterised as $[\{Pd(CO)Cl\}_n]$,[5] separated after 2 h; in the same time the absorption of CO stopped. The presence of CO_2 in the gas phase was confirmed both chemically and by i.r. spectroscopy. The precipitate was filtered off, washed with acetic acid, and kept in vacuum over NaOH. Yields were 85% based on the initial palladium acetate (130 mg).

If the reaction was carried out at higher $HClO_4$ concentration (0.25 mol dm^{-3}) yields decreased to 55% and a black precipitate, which analysed quite close to Pd(CO)Cl and which showed i.r. carbonyl bands very similar to those of $[\{Pd(CO)Cl\}_n]$ (see Results and Discussion section), separated from the mother-liquor on standing. It also showed some i.r. bands typical of $MeCO_2H$ and $HClO_4$, of variable intensities according to the different preparations. When a suspension of this black precipitate was stirred under a CO atmosphere for a few hours, only the yellowish $[\{Pd(CO)Cl\}_n]$ was obtained.

When the concentration of $HClO_4$ was increased (0.35 mol dm^{-3}) a brown-yellow precipitate was obtained (working under similar conditions) together with the same black precipitate, which separated later from the mother-liquor on standing. Analytical data suggested that the brown-yellow precipitate was a mixture of $[\{Pd(CO)Cl\}_n]$ and another palladium compound containing more chlorine.

When the reaction with CO was carried out as above, but with the $HClO_4$ concentration higher than 0.45 mol dm^{-3}, a brown precipitate separated quickly, whilst from the mother-liquor the black precipitate described above was obtained on standing. The brown precipitate (yields 50%) was soluble in aromatic solvents and analysed as $PdCl_2$. The mass spectrum confirmed that it was β-$PdCl_2$ or Pd_6Cl_{12}.[7]

Reduction of HNO_3.—To a solution of palladium acetate (300 mg) in acetic acid (30—40 cm^3), concentrated HNO_3 was added (0.25 mol dm^{-3}). The solution was stirred at 20 °C under CO (3 atm); after 2 h a brown-violet product separated, which is still under investigation. In the gas phase the typical colour of NO_2 was initially observed but after 0.5 h the gas phase was colourless. By opening the reaction vessel to air the formation of NO_2 was observed, in agreement with the presence of NO in the gas phase. If a suspension of this violet product was allowed to stay under CO for an additional hour the known compound $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$ separated in 70% yield. When the reaction was carried out at 30 °C the violet intermediate was difficult to separate and $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$ was obtained quantitatively in only 1 h. When the above reaction was carried out at 10—15 °C, NO_2 evolution was still initially observed followed by its disappearance. Under these particular conditions a few other palladium intermediates can be separated. These are under investigation. When the reaction mixture was kept under the above reaction conditions overnight a nearly quantitative separation of $[Pd_4(O_2CMe)_4(CO)_4]\cdot 2MeCO_2H$ occurred.

Reduction of H_5IO_6.—To palladium acetate (300 mg) dissolved in acetic acid (30—40 cm^3), H_5IO_6 was added in variable concentrations (0.1—0.4 mol dm^{-3}). By stirring, under 1 atm of CO and at room temperature, a black precipitate separated in 1 h at any concentration of H_5IO_6; the presence of CO_2 in the gas-phase was confirmed both chemically and by i.r. spectroscopy. The black precipitate, which analysed as PdI_2, dissolved in KI solution as expected.

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