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Platinum Bronzes

III. A Reinvestigation of the Composition of Adams' Catalyst (1)

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The platinum oxide, commonly known as Adams' catalyst and formulated as $PtO_2 \cdot H_2O$, has been found to be a mixture of Pt, α-PtO_2 (possibly hydrated) and $Na_xPt_3O_4$, sodium platinum bronze. Both α-PtO_2 and $Na_xPt_3O_4$ are active as hydrogenating agents for cyclopentene and benzene, but α-PtO_2 is converted completely to Pt metal, while only minor decomposition to the metal occurs for $Na_xPt_3O_4$. It is suggested that the irreproducibility of the activity of Adams' oxide might be caused by a variation of the relative amounts of Pt metal and the oxides in the mixture. Methods for preparing a more consistent catalyst are discussed.

More than half a century ago Adams and Voorhees (2) introduced platinum oxide as a catalyst in the reduction of organic compounds. The simplicity of the preparation and the activity of the oxide as a catalyst led to its considerable popularity, which makes it still a frequently used catalyst in synthetic organic chemistry. It is by now generally accepted that the oxide, formulated by Adams as $PtO_2 \cdot H_2O$, is not the actual catalyst, but rather a precursor to an extremely finely divided form of metallic platinum (3). Therefore, the oxide is not a catalyst, strictly speaking; it is used up in the reduction of the organic material and thus not reusable. The exact stoichiometry of this oxide has never been clearly established and seems to depend on the mode of preparation (2). In the course of an investigation of platinum bronzes (1), ternary platinum oxides with the general formula $M_xPt_3O_4$, where the counterion M is generally a group I or II cation and $0 < x < 1$, we became interested in the true nature of Adams' oxide. Inoue (4) reported some years ago that thermal degradation of PtO_2, prepared by Wöhler's (5) method, results in a material that contains besides other phases, Pt_3O_4. Recently Sukhotin and co-workers (6) reported that thermal decomposition of Adams' oxide yields Pt_3O_4 and Pt metal at temperatures above 650°C. In this note we report our results concerning the true composition of Adams' oxide and the hydrogenating activity of the individual components.

In order to try to improve the yield of Pt_3O_4 from the decomposition of Adams' oxide, we investigated this decomposition reaction in detail. X-ray powder diffraction provides a convenient way of following the reaction. Metallic platinum has its strongest peak at $2\theta = 39.8°$ [(111) reflection] (7) and α-PtO_2 gives the strongest peak at $2\theta \approx 33°$ [(100) reflection] (8). The strongest reflection for the platinum bronzes, the (110) reflection, comes around $2\theta = 35°$ (9), depending on the exact lattice parameter, which can vary by 5% with temperature and counterion.

No change in Pt_3O_4 content of the decomposition product was obtained by

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either changing the rate of heating, final reaction temperature, or the atmosphere (i.e., air or O_2). Careful X-ray diffraction of commercial "$PtO_2 \cdot H_2O$" showed three phases to be present, Pt, α-PtO_2 (probably hydrated, but still possessing the same basic structure as α-PtO_2), and Pt_3O_4. The relative percentages of these three components varied according to the source of the commercial "$PtO_2 \cdot H_2O$" (ROC, Engelhard Industries, and D. F. Goldsmith). As no increase in Pt_3O_4 content was found, it seems that no Pt_3O_4 is formed as a result of thermal decomposition of α-$PtO_2 \cdot xH_2O$ but instead only Pt metal is formed. This conclusion is supported by the fact that the relative amount of Pt metal increases with a decrease in α-$PtO_2 \cdot xH_2O$ content.

Pure Pt_3O_4 without any counterion has only been prepared under high O_2 pressures (*10*), and therefore we looked for possible counterions in the Pt_3O_4 phase contained in Adams' oxide. The presence of Na in this Pt_3O_4 phase was confirmed by a flame test and Auger spectroscopy, and the phase should thus be formulated as $Na_xPt_3O_4$. Broadline NMR on the ^{23}Na nucleus provided additional proof for the presence of Na and showed the presence of a small amount of hydrogen as well.

The reason for the presence of $Na_xPt_3O_4$ became clear when we found that $Na_xPt_3O_4$ can be prepared as follows.

$$NaNO_3 + H_2PtCl_6 \xrightarrow[\text{boil, 700°C}]{\text{air}} Na_xPt_3O_4 + Pt,$$

which is the procedure given by Adams for the preparation of his oxide, except for the fact that we boiled the melt. This way apparently all α-PtO_2 is decomposed into Pt, which can be dissolved in aqua regia to leave pure $Na_xPt_3O_4$. When Adams' oxide was prepared from KNO_3 and K_2PtCl_6 at $\sim 600°C$, only 2 phases were found, namely Pt and α-$PtO_2 \cdot xH_2O$; heating at 700°C yielded pure Pt.

The activity of Adams' oxide has been shown to depend markedly on the amount of sodium in the oxide (*11*). This sodium was thought to be present in the form of some unspecified sodium salts. We carried out some rough qualitative tests of the activity of α-PtO_2 and $Na_xPt_3O_4$ as hydrogenating agents. A 500 ml pressure bottle was filled with 80 mg of the oxide and 10 ml of deoxygenated 190 proof ethanol. After 1 ml of cyclopentene (redistilled by refluxing under N_2 pressure over potassium) or benzene (redistilled over sodium) was added, the flask was filled with Linde H_2 gas in a commercial PARR pressure apparatus. A pressure drop indicated hydrogenation. The products (cyclopentane or cyclohexane) were identified by gas chromatography and NMR. Benzene was selected as substrate, because it has been reported that only sodium-free platinum oxide (i.e., pure α-$PtO_2 \cdot xH_2O + Pt$) will hydrogenate benzene (*12*).

Well crystallized pure α-PtO_2 was prepared by the method of Hoekstra, Siegel, and Gallagher (*8*). Pure $Na_xPt_3O_4$ was obtained by the above described reaction and $NaPt_3O_4$ was prepared using the method of Scheer (*13*).

$$Na_2CO_3 + Pt(\text{black}) \xrightarrow[500\text{–}550°C]{O_2} NaPt_3O_4 + Pt.$$

Pure $NaPt_3O_4$ is isolated by boiling the reaction products in aqua regia.

All three oxides readily hydrogenate cyclopentene. α-PtO_2 was found to decompose completely to poorly crystallized metallic Pt (as judged from the width of the diffraction peaks). Only minor decomposition was observed for $Na_xPt_3O_4$ and $NaPt_3O_4$. Each of these oxides could be reused for hydrogenation and effected faster hydrogenation than an equal amount (by weight) of commercial "$PtO_2 \cdot H_2O$." We attribute this to the large amount of inactive metallic Pt already present in the commercial material. Our data do not show any significant difference in the rate of hydrogenation effected by the three pure oxides. We feel that without accurate knowledge of the relative surface areas of the oxides no meaningful comparison can be made. The particle sizes of α-PtO_2, $Na_xPt_3O_4$, $NaPt_3O_4$, and "$PtO_2 \cdot H_2O$" were 200–270, 270–400, ~400 and >400 mesh, respectively.

Use of Adams' oxide in kinetic and

selectivity studies has been complicated by the difficulties encountered in preparing an oxide that would give reproducible results (*14*). In view of the results obtained here we suggest that variations in the relative amounts of Pt, α-$PtO_2 \cdot xH_2O$, and $Na_xPt_3O_4$ can cause changes in the hydrogenating activity of the mixture. Such variations in composition can result from slight changes in rate of heating, final temperature, and heating time of a melt of $NaNO_3$ and H_2PtCl_6.

At 47 psi both $Na_xPt_3O_4$ and α-PtO_2 do hydrogenate benzene, but α-PtO_2 seems to effect faster conversion. Again all the α-PtO_2 decomposed into Pt metal while only a small amount of decomposition was found to occur for $NaPt_3O_4$ and $Na_xPt_3O_4$. In this context it is interesting to note that both Na_2PtO_3 (*13*) and $CaPt_2O_4$ (*1*) act as true hydrogenating catalysts, be it slow, for cyclopentene. No decomposition is observed for either of these oxides. On the other hand $CdPt_3O_6$ (*15*), a known hydrogenating agent, is completely converted into metallic platinum.

Adams suggested that the actual "catalyst" in the reducing process is not $PtO_2 \cdot H_2O$ but a lower oxide formed by reduction of $PtO_2 \cdot H_2O$ with hydrogen. In view of the recent results obtained by physical techniques that were not readily available to the discoverer, of this catalyst, this does not seem to be the case. Instead a lower oxide, $Na_xPt_3O_4$, is present in the actual mixture. Our results suggest that use of either α-PtO_2 or $Na_xPt_3O_4$ in a pure state will reduce the amount of oxide necessary to effect hydrogenation. Furthermore, by using the method of Scheer for the preparation of $NaPt_3O_4$ one can easily recycle any metallic Pt formed in the process by simply reheating it with an equimolar portion of Na_2CO_3 in the solid state and dissolving the unreacted metallic platinum in aqua regia.

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