Mechanism of Methanol Oxidation by Lead Tetra-acetate. The Novel Intermediacy of Formaldehyde Hemiacetal

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Summary The oxidation of methanol by lead tetra-acetate in methanol solution produces formaldehyde with C–H cleavage in the rate determining step, but the product HCHO, reportedly stable in the presence of $Pb(OAc)_4$ is further oxidized *via* the methanol hemiacetal to methyl formate.

Oxidations of primary alcohols by $Pb(OAc)_4$,[1] slow in acetic acid but fast enough for synthetic use in pyridine,[2] yield aldehydes, which are relatively stable in the presence of $Pb(OAc)_4$ with α-acetoxylation occurring *via* the enol, only on prolonged oxidation. Hence, formaldehyde is reportedly unaffected by $Ph(OAc)_4$ in non-alcoholic solvents.

Mechanistically, alcohol oxidations by $Pb(OAc)_4$ are postulated to involve initial complexation followed by a rate-determining rupture of a C–H bond at the hydroxyl bearing carbon.[1] To confirm this we now report the first quantitative primary-isotope effect for alcohol oxidation by $Pb(OAc)_4$

$$k^{\text{MeOH}}_{\text{obsd}}/k^{\text{CD}_3\text{OD}}_{\text{obsd}} = 4{\cdot}25\times10^{-5}/1{\cdot}11\times10^{-5} = 3{\cdot}8 \text{ at } 25°\dagger$$

The kinetics of methanol oxidation by $Pb(OAc)_4$ in methanol solvent follow $V = k^{\text{obsd}}_{\text{MeOH}}\,[\text{Pb}^{\text{IV}}]$ for the first 30% of the reaction. Beyond this point a rate acceleration is observed. It was confirmed by iodometric titration that the initial changes in optical density of the brown-red $Pb(OAc)_4$–methanol complex, used to monitor these reactions, were directly proportional to the concentration changes in total $\text{Pb}^{\text{IV}}, -\dfrac{d[\text{Pb}^{\text{IV}}]}{dt} = -\dfrac{d[\text{complex}]}{dt}$. Similarly, Norman[4] has also utilized a spectrophotometric technique for following $Pb(OAc)_4$ oxidations with iodometric confirmation of its validity. Further studies reveal that this rate increase can be attributed to a consecutive oxidation of the formaldehyde product. Addition of formaldehyde, mainly hemiacetal in methanol,[5] to a solution of $Pb(OAc)_4$–methanol complex produces a rapid optical density change indicative of the partial formation of a new complex. Indeed, this change does not correspond to the removal of Pb^{IV} as measured titrimetrically. Additionally, with added formaldehyde, the rate of Pb^{IV} loss is also somewhat faster (with 1·4M HCHO, $k^{\text{MeOH-HCHO}}_{\text{obsd}}/k^{\text{MeOH}}_{\text{obsd}} = 2$). Control experiments indicate that other products cannot be responsible for any rate increases.

All of the above evidence is consistent with the following Scheme:

$$\begin{array}{lcl}
\text{MeOH}+\text{Pb(OAc)}_4 & \rightleftharpoons & \text{MeO–Pb(OAc)}_3+\text{HOAc} \\
\text{MeO–Pb(OAc)}_3 & \rightarrow & \text{HCHO}+\text{HOAc}+\text{Pb(OAc)}_2 \\
\text{HCHO}+\text{MeOH} & \rightleftharpoons & \text{MeO–CH}_2\text{–OH} \\
\text{MeOCH}_2\text{OH}+\text{Pb(OAc)}_4 & \rightleftharpoons & \text{MeOCH}_2\text{O–Pb(OAc)}_3+\text{HOAc} \\
\text{MeOCH}_2\text{OPb(OAc)}_3 & \rightarrow & \text{HCO}_2\text{Me}+\text{HOAc}+\text{Pb(OAc)}_2
\end{array}$$

The Scheme predicts the formation of both formaldehyde and methyl formate. Indeed, careful v.p.c. analysis throughout the reaction confirmed the production of both compounds as well as that of acetic acid.‡ Methyl formate cannot arise from the esterification of formic acid as the latter, even if formed, would be rapidly and quantitatively oxidized by $Pb(OAc)_4$.§ The results therefore indicate that hemiacetal formation may allow for the further oxidation of aldehydes, and the possible generality of the process is under investigation.

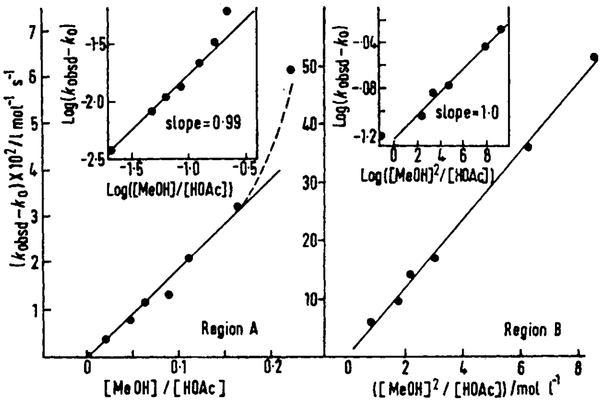

Figure. The catalytic effect of methanol on the cleavage of mandelic acid by $Pb(OAc)_4$ in acetic acid at 25·0°. For every concentration of added methanol, $V = k_{\text{obsd}}\,[\text{mandelic acid}]\,[\text{Pb}^{\text{IV}}]$ while k_0 is the observed rate constant at $[\text{MeOH}] = 0$.

Pre-equilibrium complex formation as in the above mechanistic scheme has been postulated by several workers[1] and is experimentally indicated by the colour produced when $Pb(OAc)_4$ is added to methanol, the rate reduction with added acetic acid noted above, and the disappearance of all colour on the addition of only 25% v/v HOAc. (Pb^{IV} absorbance at λ = 370nm in pure MeOH, ϵ = 1800; in 25% v/v HOAc in MeOH, ϵ = 21; in glac. HOAc, ϵ = 12). Further, Criegee has precipitated the complex, $Pb(OAc)_2(OMe)(OH)$, from $Pb(OAc)_4$ in wet methanol.[6] For simplicity we have shown only complexes of the type $ROPb(OAc)_3$ in the above scheme, but higher complexes [*e.g.*, $(RO)_2Pb(OAc)_2$] may well be important.

Such alcohol–$Pb(OAc)_4$ complexes have also been proposed as the species responsible for catalytic rate increases where in the presence of ethanol the rate of hydroperoxide decomposition was linearly dependent on alcohol concentration,[7] for glycol cleavage ractions,[8] and for methanol catalysis of mandelic acid cleavage by $Pb(OAc)_4$.[9]

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‡ Methyl formate was found in amounts between 20 and 40% of total product, depending on conditions, in contrast to the trace amounts of methyl acetate.

† The solvent deuterium isotope effect, $k^{\text{MeOH}}_{\text{obsd}}/k^{\text{MeOD}}_{\text{obsd}}$ is only 1·5 at 25°.

§ Control experiments show that formic acid oxidation by $Pb(OAc)_4$ is at least 1400 times faster than esterification by reaction with methanol solvent.

$$\mathrm{PhCH(OH)CO_2H + Pb(OAc)_4 \xrightarrow[\text{(in HOAc)}]{\text{MeOH}} PhCHO + CO_2 + (HOAc)_2 + Pb(OAc)_2}$$

A more extensive analysis of the catalytic portion of this cleavage reveals that one methanol molecule is apparently involved in the activated complex at $[\mathrm{MeOH}] < 2{\cdot}5\,\mathrm{M}$ but two methanol molecules appear to be predominantly involved at higher concentration (Figure).

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