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The Nature of the Reduction Product in Pyridinium Chlorochromate and Pyridinium Dichromate Oxidations

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The use of pyridinium chlorochromate (PCC) and. pyridinium dichromate (PDC) in the oxidation of primary and secondary alcohols has been remarkable for the selectivity and for the excellent yields in synthetic operations [1]. Anhydrous methylene chloride is the solvent of choice. The reaction results in addition to the organic product a black 'chromiumtar'. Very little attention has been given to characterise the nature of the reduction product.

Recently Brown and coworkers observed an unusual stoichiometry of 1:1 [PCC: Substrate] rather than the usual 1:1.5 in the PCC oxidation of n-octanol and trialkyl borates [2, 3]

$$RCH_2OH + C_5H_5NHClCrO_3 \longrightarrow RCHO + C_5H_5NHCl + H_2O + CrO_2 \qquad (1)$$

$$B(O{-}CH_2{-}R)_3 + 3C_5H_5NHClCrO_3 \longrightarrow 3RCHO + B(OH)_3 + 3C_5H_5NHCl + 3CrO_2 \qquad (2)$$

The 1:1 stoichiometry pointed to a net two electron reduction of Cr(VI). The reduction product was not examined in detail.

Here in this communication we wish to report that we have characterised the reduction product in PCC and PCD oxidations as stoichiometric compounds of Cr(IV) and Cr(V) respectively.

In a typical experiment 4 g of cyclohexanol (0.04 mol) in dry CH_2Cl_2 (25 ml) and PCC, (2.32 g, 0.01 mol) were refluxed for 4 h. A greyish black solid separated in addition to the chromium tar. It was filtered on a G-4 crucible, repeatedly washed with dry CH_2Cl_2 and dry ether, to remove cyclohexanone, excess of cyclohexanol and dried *in vacuo.* There was considerable loss of the reduction product due to one mole of water produced during the reaction. Yield [0.5 g, ~25%, based on PCC]. The reduction product analysed for $C_5H_5NHClCrO_2$ with respect to chromium and chlorine. The identity of the Cr(IX) state was confirmed from the following:

a) Acid dispropornation to Cr(VI) and Cr(III)

$$3Cr(IV) \longrightarrow Cr(VI) + 2Cr(III) \qquad (3)$$

In a typical iodometric estimation 0.0324 g of the compound gave a titre of 33 ± 0.1 ml of 5×10^{-3} *M* $Na_2S_2O_3$ in ten determinations. Calculations using the formula weight of 199.5 ($C_5H_5NHClCrO_2$) accounted for 97% of the active oxygen.

b) The oxidation state of Cr(IV) was further confirmed from alkaline oxidation to CrO_4^{2-} which was then estimated iodometrically in acid medium. 0.0092 g of a sample consumed 9.0 ml of $Na_2S_2O_3$ [5×10^{-3} *M*] before alkaline H_2O_2 oxidation. After oxidation to CrO_4^{2-}, the same sample consumed 27.5 ml of $Na_2S_2O_3$ [5×10^{-3} *M*].

c) The reduction product was found to be paramagnetic with a magnetic susceptibility value of 2.63 B.M. at 26 °C (determined by a Princeton Vibrating Magnetometer). This is in excellent agreement with the magnetic moment of known Cr(IV) systems like chromium tetra-tert-butoxide [4], (2.88 B.M.), consistent with the d^2 configuration.

We searched for other modified Cr(VI) reagent to see if a two electron change in CH_2Cl_2 medium is possible. Pyridinium dichromate offered such a possibility. The reduction product, a greyish black powder analyzed for the stoichiometric formula Cr_2O_5. Calculations using the formula weight of 184 accounted for more than 98% of the active oxygen.

$$Cr_2O_7^{2-}{\cdot}2C_5H_5NH^+ + C_6H_{11}OH \longrightarrow C_6H_{10}O + Cr_2O_5 + H_2O + 2C_5H_5NH^+ \qquad (4)$$

$Na_2S_2O_3$ [32.4 ml of 5×10^{-3} *M*] was consumed to titrate a sample containing 0.015 g of the reduction product directly, while 48.7 ml was required for the same amount after its oxidation to CrO_4^{2-} by alkaline hydrogen peroxide. The ratio of 1:1.5 in the two titres is consistent with the oxidation state of +5 in Cr_2O_5. The magnetic susceptibility was found to be 2.66 B.M. at 26 °C, which apparently pointed to a d^2 configuration. This magnetic moment is to be expected from a molecule having two d^1 Cr(V) centers. The only literature reference pertaining to Cr_2O_5 is seen in the work of Ward [5] who

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obtained mixed phases of Cr_3O_8, Cr_2O_5 and CrO_2 in the terminal decomposition of CrO_3 *in vacuo* and in the presence of oxygen. The ready availability of a pure Cr_2O_5 by a simple PDC oxidation of an alcohol in CH_2Cl_2 medium presents an opportunity to study its physical and chemical properties in detail. There is also a possibility that Cr_2O_5 could be a mixed valence compound of $CrO_2 + CrO_3$. An X-ray and HEPN study are in hand to descriminate between these two possibilities.

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