Short Communications

A Rapid and Selective Test for Alcohols Using the Chromium-(VI)oxide-pyridine Complex in a Glacial Acetic Acid Solution

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The chromium(VI)oxide-pyridine 1:2 complex suspended in pyridine has proved of value for effecting the oxidation of sensitive alcohols, especially in the steroid field, to the corresponding carbonyl compounds.[1,2] The complex has apparently not been used as an analytical reagent, probably because of the often low rate of reaction in the heterogeneous system. However, contrary to chromium(VI)oxide, the pyridine complex is readily dissolved by glacial acetic acid forming a brown-red solution. At room temperature, this reagent is reduced within a few minutes by most primary and secondary alcohols. The resulting, dark brown solution gives no precipitate of chromium salts on dilution with water and the oxidation products, if not too hydrophilic, are easily extracted by ethyl ether and examined for aldehydes or ketones.

A number of straight chain primary alcohols from ethanol and up to the highest member tested, stearyl alcohol, as well as 2-methyl-hexan-1-ol and 2,2-dimethyl-propan-1-ol gave clear reactions for aldehydes when treated as described below. Likewise, monofunctional secondary alcohols from C_4 and higher were easily characterized. Tertiary alcohols were not attacked by the reagent. The test has proved useful also with unsaturated or polyfunctional alcohols of aliphatic as well as of aromatic type. In some cases, however, complications occurred, due to marked hydrophilic properties of the oxidation products, to oxidative attacks at some other point in the molecule, or to a very low rate of oxidation of the alcohol group. It is safe to conclude that the pyridine complex when used in an acetic acid solution is somewhat less specific as an oxidant than when used in a pyridine medium.

Experimental. Preparation of reagent. Chromium(VI)oxide (20 g, 0.2 mole) was added in portions, with stirring, to a solution of pyridine (31.6 g, 0.4 mole) in glacial acetic acid (150 ml). The temperature was maintained at 15—20°C. The reagent was made 0.8 M in chromium(VI) oxide by dilution with glacial acetic acid to a volume of 250 ml. It proved sensitive to light and should be stored in darkness, preferably not longer than 2 months.

Qualitative test for alcohols. To 20—30 mg or 0.03 ml of the sample in a test tube is added 0.3 ml of reagent. The presence of a primary or secondary alcohol is revealed by a pronounced darkening within 1—2 min or, in rare cases, in a longer time. The brown or brown-violet solution is diluted with water (2 ml) and is extracted once with ethyl ether (0.75 ml). Part of the ethereal layer (0.1 ml) is added to 0.1 ml of a dinitrophenylhydrazine reagent[3] [2,4-dinitrophenylhydrazine (5 g) is dissolved by warming in 85 % phosphoric acid (60 ml). The solution is diluted with 96 % ethanol (40 ml) and filtered]. A yellow or red precipitate within 5 min is regarded as a positive test.

Another part of the ethereal layer (0.1 ml) is added to Schiff's fuchsin aldehyde reagent[4] (0.5 ml). The mixture is shaken for half a minute. A violet colour within 5 min indicates the presence of an aldehyde.

A more detailed report on the use of the present method and of some applications on a preparative scale will be published in the near future.

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On Equilibria in Polymolybdate Solutions

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A few years ago, we published together with Ingvar Lindqvist [1] a short preliminary report on an investigation of the equilibria $MoO_4^{2-} - H^+$ in 3 M $(Na)ClO_4$ medium at 25°C which indicated the presence of the complexes:
$HMoO_4^-$ (HL^-), H_2MoO_4 (H_2L), $Mo_7O_{24}^{6-}$ ($H_8L_7^{6-}$), $HMo_7O_{24}^{5-}$ ($H_9L_7^{5-}$) $H_2Mo_7O_{24}^{4-}$ ($H_{10}L_7^{4-}$). Afterward, we have measured data over a still broader range, and added solubility data. The "MESAK" analysis [2] of the data gave a ($\bar{p}$, $\bar{q}$) diagram which indicated strongly the presence of only mono- and heptanuclear molybdates up to a value for Z (average number of H^+ bound per L^{2-}) of around 1.4. It also gave evidence for the complex $H_{11}L_7^{3-}$ and for one larger complex. The solubility measurements indicated the presence, in acidic solutions, of a cation of charge $+1$.

The data have been treated by means of gradually improving versions of our computer program LETAGROP [3]. As a matter of fact, the difficulty of adjusting six and more equilibrium constants by simultaneous variation was one of the chief incentives for inventing LETAGROP. Since it may still take some time until we get the final resuls ready for publication and the constants have been quoted repeatedly in the meantime, we think it may be helpful to publish our present preliminary results, which may still be refined somewhat.

As usual, β_{pq} stands for the equilibrium constants for the reaction $p\ H^+ + q\ L^{2-} \rightleftharpoons H_pL_q^{(2q-p)-}$, and the limits correspond to 3σ.

> Log $\beta_{1,1} = 3.89 \pm 0.09$; log $\beta_{2,1} = 7.50 \pm 0.17$;
>
> log $\beta_{8,7} = 57.74 \pm 0.03$; log $\beta_{9,7} = 62.14 \pm 0.06$;
>
> log $\beta_{10,7} = 65.68 \pm 0.06$; log $\beta_{11,7} = 68.21 \pm 0.07$.

Among the various formulas hitherto tested for the large complex, log $\beta_{34,19} = 196.30 \pm 0.26$ gives the best agreement; however the measurements are in a fairly unfavorable range for deciding on the formula. For the cation, the agreement was improved by assuming log $\beta_{x,2} \approx 19$ (< 19.3) although this formula (*e.g.* $HMo_2O_6^+$) is not the only one possible.

A full report will be published later.[4]

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4. For references to other work on molybdate equilibria, see *Stability constants of metal-ion complexes, inorganic ligands, Chem. Soc. Spec. Publ.* **7** (1958) and **17** (1964).

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