DIFFERENTIATING BETWEEN PRIMARY, SECONDARY, AND TERTIARY ALCOHOLS

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A PRIMARY or secondary aliphatic alcohol dissolved in pure glacial acetic acid decolorizes a water solution of $KMnO_4$, while a tertiary alcohol fails to do so. A secondary alcohol will continue to react with $KMnO_4$ solution if a little concentrated sulfuric acid is added, while a primary alcohol does not. By means of these reactions one may distinguish between primary, secondary, and tertiary alcohols of the paraffin series. Further, no more than one drop of the alcohol is necessary to make the test, which fact should make it especially interesting in investigations where only small quantities of alcohol are available.

A convenient procedure is as follows: A 4-inch test tube is fitted with a one-hole rubber stopper carrying a glass rod which reaches to the bottom of the test tube. Glacial acetic acid (3 ml.) is introduced into the test tube, and then one drop of the pure unknown is added. A saturated, filtered solution of $KMnO_4$ in water is added, a drop at a time, to the contents of the tube, with stoppering and vigorous shaking between each addition.

If no decolorization of the $KMnO_4$ takes place, the alcohol is tertiary. If decolorization takes place (best ascertained from time to time by spotting the mixture by means of the glass rod onto filter paper), the addition of $KMnO_4$ is continued a drop at a time until the pink color of $KMnO_4$ persists. When decolorization

has ceased to take place a drop of concentrated H_2SO_4 is added and the addition of $KMnO_4$ with shaking is continued. If the pink color is not discharged under these conditions the alcohol is primary. If decolorization proceeds again after the addition of H_2SO_4, followed by a final permanent pink color, the alcohol is secondary.

It is advisable to run a blank test on the glacial acetic acid used, because some glacial acetic acid samples contain extraneous materials which react with $KMnO_4$ solution.

This method has been found reliable for all aliphatic alcohols through the amyl group. Whether it can be extended to other classes of alcohols has not been determined.

To a student in the laboratory it would seem that this different approach to the differentiation of the alcohols would be much more simple and direct than the Lucas test[1] currently in manuals.

[1] ADAMS, ROGER, AND J. R. JOHNSON, "Laboratory Experiments in Organic Chemistry," The Macmillan Co., New York, 1949, pp. 191–3.