Conversion of Methanol into Hydrocarbons

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Summary Heating of methanol or trimethyl phosphate in phosphorus pentoxide or polyphosphoric acid (or combinations) at 190° gave rise to a 36—39% yield of hydrocarbons made up of a complicated mixture of alkanes, cycloalkanes, and some alkenes.

THE production of hydrocarbons from alcohols other than methanol is not novel,[1] but we have found that methanol can give a fair yield of hydrocarbons. The discovery is remarkable because methanol does not form an alkene and yet must proceed from a one-carbon compound to multicarbon units. In a typical reaction, polyphosphoric acid (100 g) and trimethyl phosphate (72 ml) (or equivalent amounts of methanol and phosphorus pentoxide or other combination) were heated to 190°. During the next 4 h a colourless liquid separated which refluxed gently. If the internal temperature rose above 200°, carbonization occurred, gases were evolved, and the yield dropped. The mixture was cooled in a solid CO_2 bath, and the clear, upper layer was decanted from the frozen layer. The average yield was 9—10 g, 36—39%, based on conversion into hydrocarbons of empirical, average formula, CH_2, although formulae of the hydrocarbons ranged from C_nH_{2n+2} to C_nH_{2n-10}. The gaseous fraction was trapped on one occasion and contained dimethyl ether with other unidentified products. About 200 compounds were detected in the liquid product of which 140 were identified by g.l.c. capillary columns–mass spectrometry. The hydrocarbon distribution was as follows: C_4, 4·2; C_5, 11·8; C_6, 21·5; C_7, 27·3; C_8, 15·5; C_{9+}, 19·7%. The largest fraction, C_7, contained 2-methylhexane (6·9%), 2,3-dimethylpentane (5·1%), 3-methylhexane (6·8%), heptane (0·4%), and substituted cyclopentanes. The C_{9+} fraction contained unidentified compounds of empirical formulae C_nH_{2n-4} up to C_nH_{2n-10}. The monoaromatic compounds, C_nH_{2n-6}, were highly substituted and maximal at C_{12}. Almost all fractions contained small amounts of alkenes, *e.g. ca.* 0·6% of methylcyclohexene in the C_7 fraction. A list of other compounds identified is available from the author. If the hydrocarbon layer above the polyphosphoric acid layer was refluxed longer than 4 h, the amount of the heavier fractions increased at the expense of the lighter fractions, and the layer was oilier, slightly yellow with a hint of blue fluorescence. The g.l.c. recording of the hydrocarbons obtained from methanol contained about twice the number of peaks as that from ethanol.

The most intriguing question is how a one-carbon molecule, methanol, is converted into a two-carbon molecule, such as ethylene. The alkylations and rearrangements beyond the two-carbon stage to the hydrocarbon mixture observed are known.[2,3] Two explanations for the initial step come to mind. First, the five-co-ordinate carbon of Olah[4,5] may be invoked. The operation of this type of pathway would be noteworthy as the medium is by no means a superacid at room temperature but may become so at high temperature.[6] Alternately, the only other intermediate with sufficient energy for sp^3 carbon–hydrogen insertion is carbene which might arise by α-elimination[7] from methyl phosphate (or polyphosphate) at the high temperature of reaction.

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