The Heterogeneous Oxidation of Alkylaromatic Hydrocarbons by Potassium 12-Tungstocobaltate(III)

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HETEROPOLY-TUNGSTATES and- MOLYBDATES oxidize some oxygen- and nitrogen-containing organic compounds to give "heteropoly blues",[1] which result from the reduction of the tungstate (or molybdate) framework;[2,3] the hetero-atom is not involved. We report the heterogeneous oxidation of some alkyl aromatic hydrocarbons by solid potassium 12-tungstocobaltate(III), $K_5[Co^{III}O_4W_{12}O_{36}]$, which results only in the reduction of cobalt(III) to produce the isomorphous cobalt(II) compound[4] $K_5H[Co^{II}O_4W_{12}O_{36}]$.

The cobalt heteropoly-compounds were prepared;[5] analysis indicated the compositions to be $K_5[Co^{III}O_4W_{12}O_{36}]$,$18H_2O$ and $K_5H[Co^{II}O_4W_{12}O_{36}]$,$17H_2O$. Since both the Co^{III} and Co^{II} 18-hydrates lost only $17H_2O$ below 200°, the last H_2O being lost at *ca.* 410° (decomposition also occurred at this latter temperature) the Co^{III} monohydrate was used for the oxidations (96° for 50—200 hr.) with an excess of the pure hydrocarbons. The Co^{II} and Co^{III} contents of the solid were determined spectrophotometrically in an aqueous sodium acetate–acetic acid buffer (pH 4—6),† and the organic products were analysed by gas chromatography.

The oxidation of toluene and the three isomeric xylenes at 96 gave the following products (relative yields in parentheses; diphenylmethane isomers not given): toluene: phenyl-*p*-tolylmethane (77%), benzaldehyde (23%), and benzyl alcohol (trace); *o*-xylene: *o*-tolyl-3,4-xylylmethane (61%), *o*-tolualdehyde (33%), and *o*-tolylmethanol (6%); *m*-xylene: *m*-tolyl-3,5-xylylmethanol (67%), *m*-tolualdehyde(26%), and *m*-tolylmethanol (7%); *p*-xylene: *p*-tolyl-2,5-xylylmethanol (59%), *p*-tolualdehyde (34%), and *p*-tolylmethanol (7%). The oxidation of *p*-xylene in the presence of benzene resulted in addition to the benzene ring to give phenyl-*p*-tolylmethane (45%), *p*-tolyl-3,6-xylylmethane (36%), *p*-toluldehyde (19%), and *p*-tolylmethanol (trace).

The 12-tungstocobaltate-(III) and -(II) ions undergo ready outer-sphere electron exchange in aqueous solution[6] and oxygen exchange between solvent and framework is probably not involved. The oxidation of alkylaromatics probably occurs by outer-sphere electron transfer from the aromatic π-system with formation of the aromatic radical-cation, followed by proton expulsion to form a benzyl radical which is further oxidized to the carbonium ion in a second outer-sphere electron transfer. The existence of aromatic radical-cations as intermediates in oxidations of alkylaromatic hydrocarbons by cobalt(III) acetate in acetic acid, has recently been established,[8] and has been suggested as participating in oxidations by managanese(III)[9] and palladium(II)[10] acetates. The carbonium ion then attacks the aromatic ring to form the diphenylmethane product.

An examination of the structure of potassium 12-tungstocobaltate(III) indicates that the crystal contains channels surrounded by six hereropoly-ions.[4] A benzyl radical produced within a channel is likely to be oxidized by another ion to the carbonium ion before diffusing out of the crystal.

The side-products (alcohol and aldehyde) results from the attack of the carbonium ion on the water of hydration to form the alcohol, which is subsequently oxidized to aldehyde in a similar fashion.

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† It was found that the intensity of the visible spectrum of $K_5H[CO{\rm II}O_4W_{12}O_{36}]$ was very dependent on pH; thus a buffer was necessary for analysis.

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