# Oxidation of Saturated Hydrocarbons by Hydrogen Peroxide in Pyridine Solution Catalysed by Copper and Iron Perchlorates

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Oxidation of secondary C–H bonds of saturated hydrocarbons ($C_6H_{12}$, 2-methylbutane) by $H_2O_2$ in the presence of copper or iron perchlorates in pyridine solution yields the ketone and alcohol with alkyl radicals not being intermediates.

Recently an unusual selectivity in alkane oxidation by dioxygen has been observed in pyridine solution when carboxylic acids were present; this reagent combination is now known as the Gif-system.[1,2] The oxidation is a coupled process involving iron or zinc powder and an iron complex. There exist a few such systems, which differ from each other only in details, *e.g.*, a Hg-cathode is used as a reductant in the Gif–Orsay system.[3]

The characteristics of the systems are as follows: i, the oxidation of secondary C–H bonds yields a ketone without the intermediate formation of an alcohol;[4] ii, there are no tertiary alcohols among the products in branched alkane oxidation; iii, alkanes can be oxidized in the presence of high concentrations of extremely reactive compounds, *e.g.* aldehydes, alcohols *etc.*;[2,4,5] iv, the same coupled oxidation proceeds in pyridine with Cu, Ni and Co as well as Fe powder.[4,5]

Here we study thoroughly the possibility that alkane oxidation by hydrogen peroxide in pyridine solution is catalysed by metal ions. The oxidation was carried out in pyridine solution (3 ml) with the addition of carboxylic acids ($MeCO_2H$, $CF_3CO_2H$) or perchloric acid (in the form of $C_5H_5N{\cdot}HClO_4$ salt) (0—1.0 M). Copper and iron perchlorates were used as catalysts ($6 \times 10^{-3}$ M). The reaction began after the addition of $H_2O_2$ (30% aqueous solution) and after 2 h stirring at room temperature the products were analysed by g.l.c.

Oxidation of cyclohexane appeared to be of low efficiency, with low cyclohexanone and cyclohexanol yields, when catalysts synthesized by dissolving copper and iron powders (organoiron cluster)[1] in the pyridine–carboxylic acid solution under dioxygen were used. However, the use of simple salts, *e.g.* $Fe(ClO_4)_2{\cdot}6H_2O$ or $Cu(ClO_4)_2{\cdot}6H_2O$, as catalysts and $C_5H_5N{\cdot}HClO_4$ as an acid resulted in a large increase in the product yields, that of cyclohexanone being notably high, approaching 8—10% per $H_2O_2$ (Table 1). The main product (as in the Gif-system) was the ketone, the usual alcohol/ketone ratio being *ca.* 0.05—0.15. The product yield increased with the cyclohexane concentration, and was slightly dependent on the $C_5H_5N{\cdot}HClO_4$ concentration in the region of 0.25—1.0 M.

It is noteworthy that the alcohol is not an intermediate in the $H_2O_2$ oxidation just as in the Gif-system. For example, if cyclohexane and cyclohexanol (concentration close to the product yield) were oxidized, cyclohexanol was not consumed and its amount in the system even increased as a result of oxidation of cyclohexane (Table 1, run 8). The use of cyclohexanol as the only substrate yielded substantially less ketone (Table 1, run 10), *i.e.* cyclohexanol was barely oxidized at all to ketone under the reaction conditions. It is important that added propan-2-ol did not decrease the product yield of cyclohexane oxidation even when the propan-2-ol concentration was one-order higher than that of cyclohexane, *e.g.*, at 0.19 M $C_6H_{12}$ and 2.2 M $Pr^iOH$ the decrease constituted 30% only and the propan-2-ol was oxidized to acetone ($7 \times 10^{-2}$ M).

2-Methylbutane oxidation by $H_2O_2$ yielded 2-methylbutan-

Table 1. Oxidation of cyclohexane.[a]

| | [Substrate]/M | | [Product][b]/$\times 10^2$ M | |
|---|---|---|---|---|
| Run | [$C_5H_5N{\cdot}HClO_4$] | [Cyclohexane] | [Cyclohexanone] | [Cyclohexanol] |
| 1 | 0 | 0.16 | 0.7 | 0.1 |
| 2 | 0 | 0.31 | 2.0 | 0.05 |
| 3 | 0 | 0.62 | 2.9 | 0.2 |
| 4 | 0 | 1.05 | 3.7 | 0.3 |
| 5 | 0.10 | 0.31 | 1.5 | 0.1 |
| 6 | 0.28 | 0.31 | 1.1 | 0.1 |
| 7 | 0.56 | 0.16 | 0.38 | 0.07 |
| 8[c] | 0.56 | 0.16 | 0.40 | 0.23 |
| 9 | 0.56 | 0.31 | 0.8 | 0.1 |
| 10[d] | 0.56 | — | 0.1 | 26 |

[a] Reaction conditions: [$Cu(ClO_4)_2{\cdot}6H_2O$] = $6 \times 10^{-3}$ M; $[H_2O_2]_0$ = 0.5 M; pyridine solvent, 3 ml; 18.0 ± 0.5 °C; 2 h, air. [b] Measured by g.l.c. [c] $1.7 \times 10^{-3}$ M cyclohexanol was added before the reaction. [d] 0.28 M cyclohexanol was used as substrate instead of cyclohexane.

Table 2. [$CuClO_4$] = $6 \times 10^{-3}$ M, [$C_5H_5N{\cdot}HClO_4$] = 1.2 M, $[H_2O_2]_0$ = 0.5 M.

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $[CCl_4]^{-1}$/M$^{-1}$ | 4.2 | 3.6 | 3.2 | 2.8 | 2.5 | 1.2 | 1.0 | 0.8 | 0.6 |
| R′O/RCl | 46 | 45 | 43 | 35 | 46 | 30 | 26 | 32 | 24 |

3-one as the main product, 2-methylbutan-2-ol being formed in trace concentrations.† When 2-methylbutane was substituted for 2-methylpropane, low concentrations of t-butyl alcohol were observed in the oxidate (the reaction was carried out by bubbling 2-methylpropane into the solution, under atmospheric pressure).

Previously,[2] the formation of free secondary alkyl radicals in Gif-systems has been discounted. We obtained strong evidence for the alkyl radical not being an intermediate in cyclohexane oxidation by $H_2O_2$. We used $CCl_4$ as an alkyl radical scavenger and the stable cyclohexyl chloride was formed. If the oxidation proceeded *via* alkyl radical intermediates, two competitive reactions (1) and (2) would have taken place.

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \rightarrow \text{ketone, alcohol} \quad (1)$$
$$k \simeq 10^8\text{—}10^9\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ \text{(ref. 6)}$$

$$R^{\cdot} + CCl_4 \rightarrow RCl + {\cdot}CCl_3 \quad (2)$$
$$k \simeq 10^5\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ \text{(ref. 7)}$$

To decrease the oxygen concentration argon was bubbled through the solution before the reaction was carried out in a closed 300 ml flask. Simple estimation showed a very fast oxygen transfer from the liquid to gas phase and the oxygen evolved from $H_2O_2$ had to be in the gas phase. Hence under our conditions $CCl_4$ would have to compete with $O_2$ for an alkyl radical. Indeed, the ratio of cyclohexanone and cyclohexanol yields to that of cyclohexyl chloride (R'O/RCl) changed slightly with the increase in $[CCl_4]$. However, on the extrapolation of $[CCl_4]$ to infinity this ratio did not turn out to be zero, but equal to 20 ± 2, (Table 2). In the case of the iron salt the extrapolated ratio was 10 ± 3.[5] Thus, alkyl radicals were not formed to any extent in this process.

To explain this type of oxidation, Barton *et al.* suggested the intermediate formation of an iron–carbene species in the Gif-system.[2] We suggested an alternative mechanism,[5] which included the formation of radical cations of pyridine *N*-oxide.[8] The species could be formed, for example, in reaction (3).[5]

$$HO_2^{\cdot} + C_5H_5N \rightleftharpoons HOO^{\cdot}\ldots NC_5H_5 \xrightarrow{H^+} H_2O + C_5H_5NO^{+} \quad (3)$$

One of the probable reactions of $C_5H_5NO^+$ with hydrocarbon could be as in reaction (4).[9]

$$C_5H_5NO^+ + \text{-}(CH_2)\text{-} \rightleftharpoons C_5H_5NO^+\ldots\text{-}CH_2\text{-} \xrightarrow{O_2} C_5H_5NH^+ + \text{-}CO\text{-} + HO_2^{\cdot} \quad (4)$$

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† According to ref. 1 2-methylbutan-2-ol was not formed in 2-methylbutane oxidation in the Gif-system, whereas our attempts to reproduce this result failed. We found the formation of 2-methylbutan-2-ol at a concentration close to that of 2-methylbutanone in the Gif-system.

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