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# ON THE MECHANISM OF THE GIF SYSTEM FOR THE OXIDATION OF SATURATED HYDROCARBONS

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Abstract : The high selectivity of the Gif system for hydrocarbon oxidation is shown to depend upon the capture of tert. radicals by pyridine; the mechanism for the secondary oxidation products has only a minor radical component as judged by competitive trapping.

The Gif system for the oxidation of saturated hydrocarbons consists of pyridine-acetic acid containing a soluble iron compound as a catalyst with zinc as a source of electrons and oxygen as oxidant.[1]

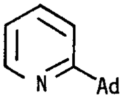
We have now shown (by isolation) that the iron compound present in this mixture is a derivative of ortho-dipyridyl. This type of iron$^{II}$ derivative can replace the iron complex used before and gives identical results. Indeed iron$^{II}$ is a catalyst for the formation of ortho-dipyridyl in the reduction of pyridine with zinc.

The most interesting features of this system are its relative efficiency, its selectivity towards saturated hydrocarbons and its selective oxidation of secondary positions to ketones in preference to oxidation of primary groups and (especially) of tertiary positions.

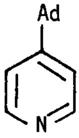
We have recently shown[2], using the hydrocarbon adamantane, that the selectivity for secondary over tertiary oxygenation increases as the concentration of oxygen is reduced and as the rate of agitation is slowed.

We are now in a position to explain the origins of this selectivity and to present a working hypothesis on the mechanism of action of the Gif system. An examination (by h.p.l.c.) of the basic fraction has shown (Table) the presence of three major compounds with an admantane skeleton coupled to pyridine. In order of importance these are 2'-

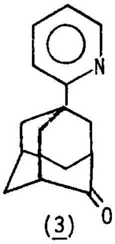
pyridyl-1-adamantane (1), 4'-pyridyl-1-adamantane (2) and the ketone (3). Authentic specimens were synthesised for comparison. Taking these compounds and the recovered adamantane into account a good mass balance is observed in the reaction (92%).



(1)



(2)



(3)

(Ad = adamantanyl-1)

Of major importance is the fact that the increased selectivity with respect to the secondary positions obtained by lowering the oxygen pressure is due to an increase in tertiary substituted compounds (1), (2) and (3).

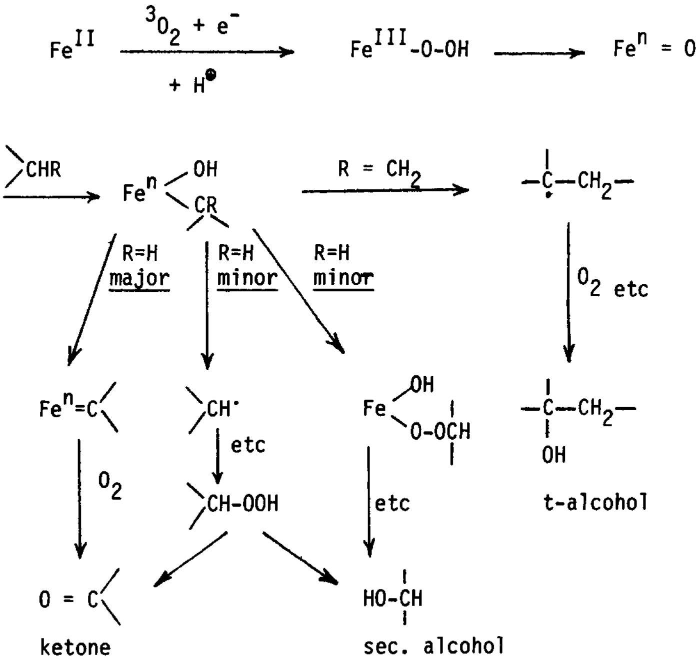
In the Table we report data for a high $C^2/C^3$ experiment (low oxygen pressure:6% $H_2O$) and for a low $C^2/C^3$ experiment (high oxygen pressure) both giving almost identical total % oxidation. The major difference is in the coupled products. If secondary radicals were also a major pathway for oxidation, $C^2/C^3$ should not vary with oxygen pressure, it being known that primary and tertiary (and by implication secondary) radicals have similar reaction rates towards pyridine.[3] Since we have demonstrated a competition between oxygen and pyridine for tertiary positions, we propose that tertiary products arise from tertiary radical chemistry and secondary products come from a different mechanism.

Finally, an overall $C_2/C_3$ can be calculated as 1.14 and 1.16 respectively. These numbers are not far from the values expected of a radical reaction.[2] Since, however, there is little evidence of secondary radical capture by pyridine we seek a different explanation. The Scheme is a working hypothesis which accounts for the unique selectivity by supposing an insertion step for the formation of a $\sigma$ Fe-C bond.

We have also determined the isotope effect ($k_H/k_D$) for the competitive oxidation of equal amounts of cyclohexane and of perdeuteriocyclohexane. A value of 2.51 was observed for the two ketones (16%) and a value of 2.50 using the ratio of recovered non-deuterated and deuterated substrates. This value differs from that found with the $Fe^V$ models.[4,5] It is comparable, however, with a number of non-porphyrin based systems.[6] It is not comparable also to values based on alkoxy or peroxy radical chemistry.[7]

In a typical oxidation of cyclohexane by the Gif system (as in high value $C^2/C^3$ adamantane oxidation) 0.7% cyclohexanol and 17.5% of cyclohexanone were formed. From the basic fraction there was isolated by h.p.l.c. 2-pyridylcyclohexane (1.6%) and 4-pyridylcyclohexane (0.6%). Both compounds were compared with authentic specimens.

This again suggests a minor participation of secondary radicals in the reaction.



Scheme

(For convenience ligands are omitted ; n is variable).

Table

| Entry | Rxn. conditions | Adamantan- | | | | | | | | $C^2/C^3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1-ol | 2-ol | 2-one | Total | $C^2/C^3$ a) | (1) | (2) | (3) | Overall |
| 1 | Aq .pyridine<br>slow stirring<br>open air, 20°C | 0.8<br>0.016 | 0.9<br>0.018 | 16<br>0.32<br>mmoles | 17.7%b)<br>0.354 | 21.1 | 6.7<br>0.134 | 6.0<br>0.120<br>mmoles | 1.2%<br>0.024 | 1.14 |
| 2 | Flow of $O_2$,<br>pyridine, 20°C | 3.9<br>0.078 | 1.5<br>0.03<br>mmoles | 13<br>0.26 | 18.4%<br>0.368 | 3.7 | 3.8<br>0.076 | 3.7<br>0.074<br>mmoles | 1.1%<br>0.022 | 1.16 |

a) $C^2/C^3$ = total of secondary products divided by tertiary product(s).

b) 2 mmoles of adamantane were oxidised as in Reference 2.

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