**SHORT PAPER**

# Oxidative functionalisation of ethane with hydrogen peroxide catalysed by chromic acid[†]

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Chromic acid catalyses efficiently (turnover numbers attain 620) the oxidation of alkanes including the very inert ethane by $H_2O_2$ or *tert*-BuOOH in acetonitrile solution at 60 °C; alkyl hydroperoxides, ketones (aldehydes) and alcohols are the main products.

Chromium complexes are known to catalyse the oxidation of various organic derivatives (see refs 1–4) particularly C–H compounds (see refs 5–13). It should be noted that compounds containing "activated" benzylic groups[8,10,11,13] or tertiary C–H bonds (*e.g.*, adamantane)[9] and methylbenzenes[12] were used as substrates; molecular oxygen, peroxides, iodosobenzene were employed in these reactions as oxidising reagents. It has been shown[14,15] that also the relatively inert cyclohexane can be oxidised by hydrogen peroxide at room temperature when a Cr(VI) oxocomplex is used as the catalyst, however the product yields were very low (the total concentration of products did not exceed 0.015 mol/dm$^3$ after 7 days, corresponding to a turnover number, TON, of *ca* 30). On the other hand, the selective functionalisation of saturated hydrocarbons, especially of the very inert light alkanes (ethane and methane), under mild conditions remains a challenging problem for metal complex catalysis.[5–7]

$$CH_3CH_3 + H_2O_2 \rightarrow CH_3CH_2OOH + CH_3CHO +$$
$$CH_3CH_2OH + CH_3COOH \quad (1)$$
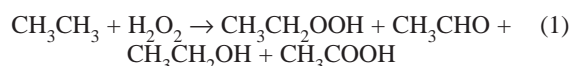
Herein we report that chromic acid catalyses the oxidation of the alkanes with hydrogen peroxide under mild conditions; the reaction is particularly efficient for the very inert ethane: $CH_3CH_3$ is oxidised by $H_2O_2$ in acetonitrile solution containing catalytic quantities of $H_2CrO_4$ at 60 °C to give ethyl hydroperoxide, acetaldehyde, ethanol and acetic acid (reaction 1), the total turnover number being 620 after 1 hour and the maximum yield equals 21% based on $H_2O_2$ (Table 1, entry 3). It follows from Table 1 that the relative content of these products depends on the initial concentration of hydrogen peroxide; at high concentrations of it, acetaldehyde becomes a predominant product. It is necessary to note that acetic acid under the conditions used is also produced via the hydrolysis of acetonitrile, however, the blank experiments demonstrated that the concentration of $CH_3COOH$ formed from $CH_3CN$ was only 0.002 mol/dm$^3$. Propane under analogous conditions (but at lower pressure, 5 bar) gave (concentrations are indicated in parentheses, mol/dm$^3$) $CH_3CH_2CHO$ (0.009), $CH_3COCH_3$ (0.026), $CH_3CH(OH)CH_3$ (0.031), $CH_3CH_2CH_2OH$ (0.02) and $CH_3CH_2COOH$ (0.009) (TON 190). Butane (atmospheric pressure, 1 bar) gave $CH_3(CH_2)_2CHO$ (0.0003), $CH_3COCH_2CH_3$

(0.0052), $CH_3CH(OH)CH_2CH_3$ (0.012), $CH_3(CH_2)_2CH_2OH$ (0.0011) and $CH_3(CH_2)_2COOH$ (0.00037) (TON 38).

The oxidations of ethane and other gaseous alkanes were carried out at 60 °C in a stainless steel autoclave (the volume of the reaction solution being 10 ml, the total autoclave volume being 100 ml). The oxidations of higher hydrocarbons were carried out in air in thermostated (60 °C) Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 10 ml. In all experiments, a 35% aqueous solution of hydrogen peroxide ("Fluka") or 70% aqueous solution of *tert*-butyl hydroperoxide ("Fluka") was used. The catalyst, $H_2CrO_4$, usually employed in concentration $5.0 \times 10^{-4}$ mol/dm$^3$, was introduced into the reaction mixture in the form of a stock solution (0.1 ml), which has been prepared by dissolving $CrO_3$ (0.025 g) in $H_2O$ (5 ml). The samples of the reaction solutions were analysed by GC (DANI-86.10; fused silica capillary column) twice: before and after addition of an excess of solid triphenylphosphine. Triphenylphosphine reduces hydrogen peroxide to water and the alkyl hydroperoxide to the corresponding alcohol which allowed the determination of the *real* concentrations of the alkyl hydroperoxide, formed from the alkane, as well as those of the alcohol and the ketone (or aldehyde). In some cases, it is possible to find peaks corresponding to alkyl hydroperoxides. These peaks disappear completely after the treatment of the solution with PPh$_3$, while peaks of the corresponding alcohols grow (see ref. 19). We have developed and used this method[5,6,16–21] for the analysis of reaction mixtures obtained from various alkane oxidations.

In order to get a mechanistic understanding of this reaction, we also studied the oxidation of higher alkanes with hydrogen peroxide in the presence of chromic acid. The main product of cyclooctane oxidation was the alkyl hydroperoxide which gradually decomposed to give predominantly cyclooctanone. The reaction was accelerated but insignificantly (*ca* 15%) if pyridine was added (see ref. 22). After 8 hours the turnover number attained 280. During the oxidation with *t*-BuOOH, the concentration of cyclooctyl hydroperoxide was low and the reaction mixture contained cyclooctanone produced with high selectivity. In this case the rate of the reaction and the product yields were somewhat lower if pyridine was added. The oxidation with $H_2O_2$ in $CH_3COOH$ as a solvent is less efficient (0.011 and 0.024 mol/dm$^3$ of cyclooctanone and cyclooctanol, respectively, after 7 hours at 60 °C and after treatment with PPh$_3$).

The oxidation of *n*-octane in $CH_3CN$ under the same conditions with $H_2O_2$ in the absence of pyridine gave after 3 h (after reduction with PPh$_3$; the concentrations are indicated in parentheses, $c \times 10^2$ mol/dm$^3$) octanal (0.17), octanone-1 (0.39),

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**Table 1**  Ethane oxidation with $H_2O_2$ in $CH_3CN$ catalysed by $H_2CrO_4$[a]

| Entry | $[H_2O_2]_0$, mol/dm$^3$ | Products, mol/dm$^3$ | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | | $CH_3CH_2OOH$ | $CH_3CHO$ | $CH_3CH_2OH$ | $CH_3COOH$ | TON[b] |
| 1 | 0.6 | 0.09 | 0.003 | 0.01 | 0 | 206 |
| 2 | 1.2 | 0.08 | 0.09 | 0.06 | 0.02 | 500 |
| 3 | 2.4 | 0.07 | 0.16 | 0.06 | 0.02 | 620 |

[a]Conditions: ethane, 30 bar; $H_2CrO_4$, $5 \times 10^{-4}$ mol/dm$^3$; 1 hour at 60°C. The concentrations of reaction products were measured before and after reduction with $PPh_3$ to determine *real* concentrations of ethyl hydroperoxide, ethyl alcohol and acetaldehyde.
[b]Turnover number, *i.e.*, total number of moles of all products per one mole of the catalyst.

**Table 2**  Selectivities of alkane oxidations by "ROOH – $H_2CrO_4$" and some other systems in MeCN[a]

| Entry | System | Alkane oxidised (the selectivity parameter [b]) | | |
| --- | --- | --- | --- | --- |
| | | *cis*-Decalin (*t/c*) | *trans*-Decalin (*t/c*) | Adamantane (3°: 2°) |
| 1 | $H_2O_2$ – $H_2CrO_4$ (60 °C) | 3.9 | 4.3 | 1.4 |
| 2 | *t*-BuOOH – $H_2CrO_4$ (50 °C) | 4.3 | 6.1 | 4.0 |
| 3 | $H_2O_2$ – *hν* ( (20 °C) | 1.3 | 2.7 | 0.9 |
| 4 | *t*-BuOOH – *hν* (20 °C) | 5.1 | 4.4 | 1.1 |
| 5 | $H_2O_2$ – $VO_3^-$ – PCA[c] | 2.1 | 2.4 | 0.7 |
| 6 | $H_2O_2$ – Mn(IV)[d] – $CH_3COOH$ | 0.12 | 33.4 | 2.0 |

[a]The concentrations of reaction products were measured after reduction with $PPh_3$. [b]Parameter *t/c*=[*trans*-decal-9-ol]/[*cis*-decal-9-ol], *i.e.*, the ratio of concentrations of *trans*-decal-9-ol and *cis*-decal-9-ol formed in the oxidation of isomeric decalins. Parameter 3°: 2° is normalised (*i.e.*, calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms at tertiary and secondary carbons, respectively. [c]PCA, pyrazine-2-carboxylic acid. For this system, see refs 16, 19. [d]Complex LMn$^{IV}$(O)$_3$Mn$^{IV}$L, where L = 1,4,7-trimethyl-1,4,7-triazacyclononane. For this system, see refs 20, 21.

octanone-3 (0.44), octanone-2 (0.36), octanol-4 (1.65), octanol-3 (1.8), octanol-2 (2.0), octanol-1 (0.5). Taking into account only concentrations of alcohols, we can calculate the non-normalised ratio C(1) : C(2) : C(3) : C(4), *i.e.*, relative reactivities of hydrogens at 1, 2, 3 and 4 carbon atoms of the alkane chain, respectively: 1.0 : 4.0 : 3.6 : 3.3. This selectivity is higher than that obtained by us for the oxidation with the system $H_2O_2$ – *hν* (1.0 : 2.8 : 2.9 : 2.7)

Selectivity parameters for the oxidation of decalin (*cis*- and *trans*-isomers) and adamantane are given in Table 2. It can be seen that selectivities for the two Cr-containing systems (entries 1 and 2) are different from those obtained for HO-radical-generating systems (entries 3 and 5) and from the system capable of generating HO and *t*-BuO radicals (entry 4). It should be noted, that the Cr-containing systems oxidise non-stereoselectively unlike the Mn(IV)-based system recently described (entry 6). Thus one can conclude that the Cr-catalysed reactions does not seem to proceed via HO radicals but involve possibly peroxo complexes[23-25] as oxidising species.

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