Organic Chemistry

Oxidation by a "H_2O_2–vanadium complex–pyrazine-2-carboxylic acid" reagent

5.* Oxidation of lower alkanes with the formation of carbonyl compounds

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Lower alkanes (ethane, propane, *n*-butane, *n*-pentane) are readily oxidized in acetonitrile solvent by H_2O_2 with vanadate anion – pyrazine-2-carboxylic acid (PCA), as the catalyst at 75 °C and pressures of ~3 atm to produce predominantly or exclusively ketones (aldehydes). Isobutane is transformed selectively into *tert*-butyl alcohol. The oxidation of cyclohexane at 26 °C in acetone or acetic acid is less efficient than in acetonitrile. The reaction does not occur in *tert*-butyl alcohol.

Key words: metal complex catalysis, oxidation, hydrogen peroxide, vanadium complexes, alkanes, activation of the C–H bond.

Recently, much attention has been paid to the oxidation of organic compounds and especially hydrocarbons by molecular oxygen and hydrogen peroxide since these oxidizing reagents are inexpensive and produce only water as a by-product.[2–5] Reactions involving hydrogen peroxide are catalyzed by various transition metal complexes (see Refs. 6–13). Vanadium complexes are known to play an important role in chemical as well as biological oxidations,[14,15] and have been used as catalysts in the oxidation of hydrocarbons by hydrogen peroxide.[16–24] Earlier it was shown that a vanadium complex in the presence of pyrazine-2-carboxylic acid (PCA) catalyzes rapid oxidation of hydrocarbons and other organic compounds (*e.g.*, alcohols) with 30% aqueous hydrogen peroxide in acetonitrile.[1,25–28] Since benzene, *n*-hexane, *n*-heptane, 2-methylhexane, 3-methylhexane, and cyclohexane were used as substrates, these oxidations were carried out in open vessels in air at 20–70 °C. At low temperature, the corresponding alkyl hydroperoxide was the predominant product. This hydroperoxide slowly decomposed to produce the respective ketone and alcohol. The study of oxidation of saturated hydrocarbons by H_2O_2 in the presence of the vanadate–PCA catalyst was extended to lower alkanes as substrates and solvents other than acetonitrile.

Experimental

The oxidation of lower alkanes were carried out in closed 250 mL Pyrex cylindrical vessels with vigorous stirring at constant temperature. The volume of the reaction solution was 50 mL. Initially, 0.4 mL ($6.7 \cdot 10^{-3}$ mol) of a 50% aqueous

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* For Part 4, see Ref. 1.

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solution of hydrogen peroxide (Fischer) was added to the solution of the catalyst (in all cases $5 \cdot 10^{-6}$ mol of n-Bu_4NVO_3 and $2 \cdot 10^{-5}$ mol of PCA in 50 mL of MeCN). Then 5 mL of pentane was added to the solution and the vessel sealed with a pressure head containing a pressure gauge. With gaseous alkanes, the reaction mixture comprised 50 mL of acetonitrile containing the same amount of H_2O_2 and the catalyst as above, and 2.8 atm (0.28 MPa; $2.5 \cdot 10^{-2}$ mol)(in some cases 1.4 atm; 0.14 MPa) of gaseous hydrocarbon (air was not removed from the reaction vessel prior to charging with the gaseous alkane). The temperature of the reaction was maintained at 75–77 °C. Following completion of the process, the vessel was cooled with ice and opened. The reaction of cyclohexane was carried out at 26 °C in various solvents in a cylindrical Pyrex vessel in air under vigorous stirring, and the total volume of the reaction solution was 10 mL.

The reaction mixtures were analyzed by means of GLC (each sample was analyzed twice, *viz.*, before and after addition of an access of solid triphenylphosphine). For the analysis, a Hewlett Packard Series II, 5890 chromatograph equipped with a FID detector and an HP 50 column (30 m×0.53 mm) packed with cross-linked 50% PhMe Silicone 1 μm film thickness or a 30 m Altech RSL 160 column (5 μm thickness) was used. The carrier gas was helium. A Hewlett Packard 3396 Series II integrator was employed.

Acetonitrile was distilled from CaH_2. Pentane and cyclohexane (Aldrich) were treated with H_2SO_4, washed with water, and distilled. Gaseous alkanes were used without additional purification.

Results and Discussion

In the present paper we wish to report the first results of oxidation of lower alkanes by the reagent "H_2O_2—vanadium complex—PCA" at 75 °C. at ~3 atm pressure.

When heated in the acetonitrile solution in a closed vessel, n-pentane is oxidized by the catalytic system exclusively to pentan-2-one and pentan-3-one. A solution of pentane ($4.4\ 10^{-2}$ mol) was heated at 77 °C for 1 hour in a closed vessel containing H_2O_2 and 200 mL of air in the gas phase to yield $1.8 \cdot 10^{-3}$ mol of pentan-2-one and $1.1 \cdot 10^{-3}$ mol of pentan-3-one. The total number of catalytic cycles was 580 for this reaction. In analogous conditions, reaction at 75 °C for 5 hours produced $2.2 \cdot 10^{-3}$ mol of pentan-2-one and $1.3 \cdot 10^{-3}$ mol of pentan-3-one. In this case, the total number of catalytic cycles was 700, and the relative reactivities of hydrogen atoms at carbon atoms 2 and 3 of n-pentane were *ca.* C(2) : C(3) = 1 : 1. The comparison with the amounts of the two main ketones, the yields of the products of oxidation of methyl groups as well as alcohols formed were much lower than those of ketones and were not determined. No pentyl hydroperoxide was present in the reaction mixture, since the chromatograms of the samples before and after reduction with triphenylphosphine were similar (see, *e.g.*, Ref. 1). It should be noted that the reaction is highly efficient with respect to hydrogen peroxide: two molecules of H_2O_2 produce one molecule of pentanone. The molecular oxygen present in the gas phase in the reaction vessel can take part in oxidation of the hydrocarbon.

Isobutane ($1.2 \cdot 10^{-2}$ mol; 75 °C; 2.5 h) was oxidized to produce *tert*-butyl alcohol ($6.0 \cdot 10^{-4}$ mol; 120 catalytic cycles). Acetone was not formed. In analogous conditions, n-butane gave ethyl methyl ketone, exclusively. Propane ($2.5 \cdot 10^{-2}$ mol) was oxidized (75 °C; 1 h) in acetone ($9.5 \cdot 10^{-4}$ mol; the number of cycles was 190) as the sole product detected by GLC.

The following results were obtained when ethane ($2.5 \cdot 10^{-2}$ mol; 75 °C) was oxidized by the reagent under discussion (the quantities of products in the samples before reduction with triphenylphosphine ($\times 10^4$ mol) are listed; the numbers of cycles are given in parentheses):

Product	1 h	2.5 h
Ethanol	0.8 (16)	1.3 (27)
Acetaldehyde	3.1 (62)	10.0 (200)
Acetic acid	4.0 (80)	7.5 (150)

The total numbers of cycles were 158 and 377 after 1 and 2.5 hours, respectively. It is noteworthy that the amounts of products obtained after 2.5 h were almost unchanged on treatment with triphenylphosphine, whereas the distribution of the products in the 1-h sample before reduction with triphenylphosphine (see Table above) differs from that in the sample after reduction (ethanol, $1.5 \cdot 10^{-4}$ mol, 30 cycles; acetaldehyde, $2.3 \cdot 10^{-4}$ mol, 46 cycles; acetic acid, $4.0 \cdot 10^{-4}$ mol, 80 cycles). This indicates (see, *e.g.*, Ref. 1) that ethyl hydroperoxide is present in the reaction solution after oxidation for 1 h.

It can be concluded that lower alkanes are efficiently oxidized by the reagent "H_2O_2—vanadium complex—PCA" in acetonitrile, and the main products are carbonyl derivatives (ketones, aldehydes or carboxylic acids). These compounds are probably formed from alkyl hydroperoxides, the primary reaction products. The mechanism of the process, especially of the latter reaction, is not completely clear. We assume that the reaction of the vanadium complex with hydrogen peroxide results in generation of hydroxyl radicals which attack the hydrocarbon, removing a hydrogen atom and producing alkyl radicals. Alternatively, the high oxidation-state vanadium complex abstracts a hydrogen atom from the hydrocarbon. The alkyl radicals thus formed react rapidly with oxygen molecules to give alkylperoxy radicals. These radicals can be transformed into alkyl hydroperoxide or a carbonyl compound (ketone or aldehyde). Apparently, the vanadium complex participates in these transformations. The accelerating role of PCA in accumulation of alkyl hydroperoxide and its involvement decomposition of the latter must also be elucidated. It should be noted that iron complexes with various chelating ligands have been shown to induce ketonization of the CH_2 groups in alkanes under the action of hydrogen peroxide.[4,5,9,10]

It was important to examine the possibility of using other solvents in oxidation. For this purpose, cyclohexane was chosen as a substrate and oxidation was carried out at 26 °C in open Pyrex vessels. If acetonitrile was used as the solvent, the oxidation of cyclohexane (concentration 0.46 mol L^{-1}) by the reagent under discussion (0.1 mmol L^{-1} of *n*-Bu_4NVO_3, 0.4 mmol L^{-1} of PCA and 0.15 mol L^{-1} of H_2O_2 as 50% aqueous solution) yielded cyclohexanone (11.3 mmol L^{-1}) and cyclohexanol (30.0 mmol L^{-1}) after 24 hours. Under the effect of triphenylphosphine, the composition of the reaction mixture changed (2.3 mmol L^{-1} of cyclohexanone and 43.0 mmol L^{-1} of cyclohexanol), indicating that cyclohexyl hydroperoxide is the main product. Prolonged (72 h) stirring of the reaction mixture yielded ketone (15.0 and 4.0 mmol L^{-1} before and after reduction with triphenylphosphine, respectively) and alcohol (60.0 and 75.0 mmol L^{-1}).

The reaction proceeds more slowly and the yields of products are lower when acetone is used as the solvent. In fact, in the same conditions, only 3.2 mmol L^{-1} of cyclohexanone and 1.5 mmol L^{-1} of cyclohexanol were formed (0.8 and 3.6 mmol L^{-1}, respectively, after reduction with triphenylphosphine). The concentrations of the products after 72 hours are also relatively low (5.2 mmol L^{-1} of ketone and 4.9 mmol L^{-1} of alcohol before reduction; 2.0 and 9.0 mmol L^{-1} after reduction). Only trace amounts of products are detected in the absence of PCA in the reaction mixture.

Oxidation reaction is also less efficient in acetic acid, and the reaction rate is only 1.5 times higher when PCA is present in the reaction solution. Only traces of cyclohexanone and cyclohexanol were detected by GLC when *tert*-butyl alcohol was employed as the solvent. Thus it can be concluded that acetonitrile seems to be the solvent of choice for oxidation of alkanes by the reagent under consideration.

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