Oxidation with the H_2O_2—VO_3^-—pyrazine-2-carboxylic acid reagent

2.* Oxidation of alcohols and aromatic hydrocarbons

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Aromatic hydrocarbons are oxidized with hydrogen peroxide in the presence of catalytic amounts of VO_3^- and pyrazine-2-carboxylic acid into phenols (provided excess hydrocarbon is used) or into quinones (at high H_2O_2 concentrations). 2-Propanol, ethanol, cyclohexanol, and benzyl alcohol are transformed into the corresponding aldehydes and ketones under the same conditions (without a solvent or in MeCN).

Key words: oxidation, hydrogen peroxide, vanadium complexes; aromatic hydrocarbons; alcohols.

The oxidation of organic compounds with hydrogen peroxide is effectively catalyzed by different complexes of transition metals.[2–9] Peroxides are known to oxidize alcohols[5,10] and aromatic hydrocarbons[11–17] in the presence of some vanadium complexes or peroxocomplexes. Previously, we have shown that the

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*For part 1, see ref. 1.

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H_2O_2—$(Bu_4N)VO_3$—pyrazine-2-carboxylic acid (PCA) system efficiently oxidizes saturated hydrocarbons mainly to give alkylhydroperoxides.[1] The present work continues the study of this system in order to use it for the oxidation of alcohols and aromatic hydrocarbons.

Experimental

The oxidation of alcohols and aromatic hydrocarbons was carried out at constant temperature in cylindrical glass vessels equipped with reflux condensers, with intense stirring (magnetic stirrer). The total volume of the reaction solution was 5 mL; the temperature was 50 °C. The yield of the products of the oxidation of alcohols and benzene was determined by means of GLC (LHM-80/6 chromatograph with flame-ionization detector, stainless steel column 1 m in length and 4 mm in diameter, Inerton AW-HMDS 0.315—0.320 mm sorbent with 5 % Carbowax 20M, argon as the carrier gas). Quinones were isolated by TLC on Silufol UV-254 plates (hexane — methylene chloride, 5 : 1 (v/v) as the eluent) and weighed.

Oxidation of anthracene. A solution of anthracene (38 mg), a 30 % aqueous solution of H_2O_2 (0.2 mL), $(Bu_4N)VO_3$, and PCA (the components of the catalyst were taken as two starting solutions with known concentrations) in MeCN (the total volume of the solution was 5 mL; the concentrations of anthracene, H_2O_2, $(Bu_4N)VO_3$, and PCA were 0.04 *M*, 0.42 *M*, 1 · 10—4 *M*, and 4 · 10—4 *M*, respectively) was heated at 40 °C and stirred for 6 h. The solvent was distilled off under reduced pressure, and the residue was chromatographed on a silica gel column with benzene as the eluent. The yield of 9,10-anthraquinone was 39 mg (79 %).

Results and Discussion

As was mentioned in our previous work,[1] the described reagent is able to oxidize benzene to phenol when the concentration of the starting phenol is markedly higher than that of hydrogen peroxide. Figure 1 shows the kinetics of phenol accumulation. Toluene gives a mixture of isomeric cresols in the ratio *meta* : *ortho* : *para* = 54 : 12 : 34. We succeeded in carrying out a deeper oxidation by using an excess of H_2O_2 and increasing the reaction time (0.22 *M* benzene, 0.42 *M* H_2O_2, $1 \cdot 10^{-4}$ *M* $(Bu_4N)VO_3$, and $4 \cdot 10^{-4}$ *M* PCA, 50 °C, 12 h): *p*-benzoquinone was formed as the main product (14 % with respect to benzene). In addition, TLC showed that *o*-benzoquinone and other unidentified products were also formed in this reaction in lower amounts. It should be noted that oxidation of hydroquinone under the above conditions (for 25 h) resulted in *p*-benzoquinone in only 2 % yield. Naphthalene (0.03 *M*) dissolved in MeCN in the presence of H_2O_2 (0.42 *M*), $(Bu_4N)VO_3$ ($1 \cdot 10^{-4}$ *M*), and PCA ($4 \cdot 10^{-4}$ *M*) was oxidized over 12 h mainly to 1,4-naphthoquinone (38 % with respect to naphthalene). Other isomeric naphthoquinones were also formed in markedly lower amounts. Finally, anthracene was readily oxidized to 9,10-anthraquinone in a good yield (79 %).

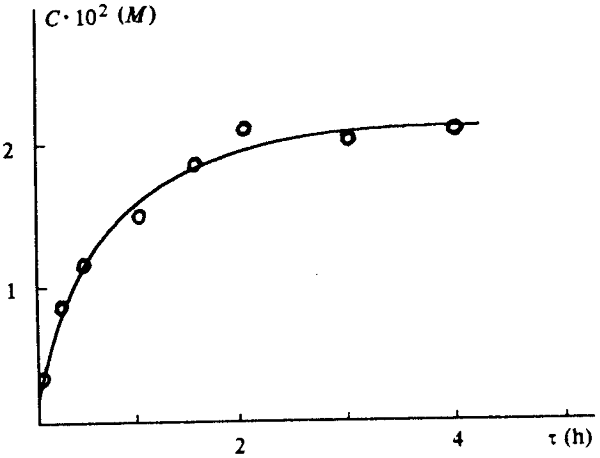

Fig. 1. Kinetic curve for phenol accumulation upon the oxidation of benzene (1.0 *M*) in MeCN with hydrogen peroxide (0.2 *M*) catalyzed by $(Bu_4N)VO_3$ ($1 \cdot 10^{-4}$ *M*) and PCA ($4 \cdot 10^{-4}$ *M*) at 50 °C.

Oxidation of alcohols was usually carried out under the conditions in which the oxidized substrate served as the solvent. Hydrogen peroxide was used in the form of 20 % and 36 % aqueous solutions.

Oxidation of 2-propanol to acetone was studied in the most detail (Fig. 2). When a 20 % H_2O_2 solution was used, the reaction ceased after 4 h when the hydrogen peroxide was completely consumed. In this case approximately 1 mole of acetone per 2 moles of H_2O_2 was formed. The addition of a new portion of H_2O_2 allowed continuation of the oxidation process. It is worth noting that in the absence of PCA as a cocatalyst, oxidation of 2-propanol proceeded very slowly; moreover, the plot of oxidation rate *versus* PCA concentration passes through a maximum (Fig. 2, *b*). We measured the rates of oxidation at 50 °C, 36 °C, and 20 °C under the same conditions and estimated the effective activation energy as 100 kJ mol^{-1}. When a more concentrated (36 % H_2O_2) solution was used, an increase in the oxidation rate was achieved.

The oxidation of primary alcohols was studied for the example of ethanol. This alcohol was slowly oxidized at 20 °C to acetaldehyde (0.11 *M* H_2O_2, $1 \cdot 10^{-4}$ *M* $(Bu_4N)VO_3$, and $4 \cdot 10^{-4}$ *M* PCA in ethanol): a $2.5 \cdot 10^{-4}$ *M* solution of acetaldehyde was formed in 70 h. At 50 °C, the reaction solution contained $0.9 \cdot 10^{-2}$ *M* acetaldehyde after 2 h.

Figure 3 demonstrates the kinetics of the oxidation of benzyl alcohol to benzaldehyde and cyclohexanol to cyclohexanone; the oxidation was carried out in MeCN.

Thus, this work showed the possibility of oxidizing aromatic hydrocarbons to phenols and quinones as well as alcohols to ketones and aldehydes using hydrogen peroxide with the $(Bu_4N)VO_3$—PCA reagent as the cata-

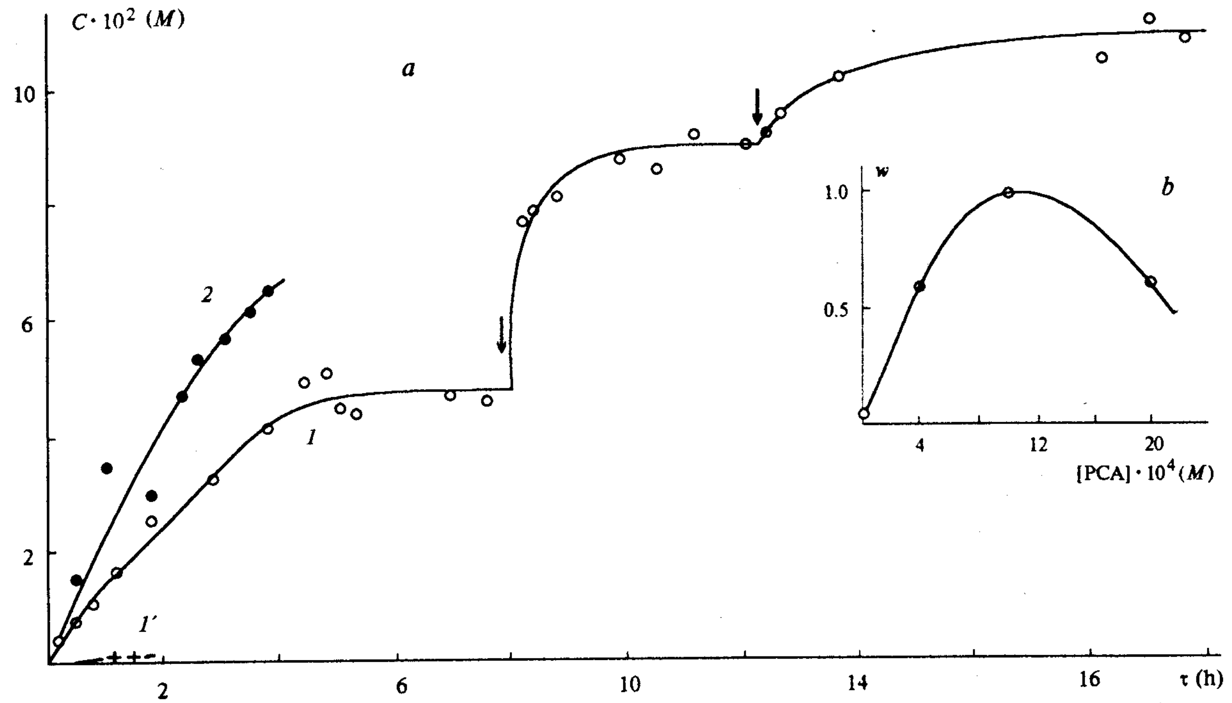

Fig. 2. Kinetic curves for acetone accumulation (*a*) and the dependence of the relative rate, *w*, of acetone accumulation on PCA concentration (*b*) upon the oxidation of 2-propanol with hydrogen peroxide catalyzed by $(Bu_4N)VO_3$ ($1\cdot10^{-4}$ *M*) and PCA at 50 °C. *a*: [PCA] = $4\cdot10^{-4}$ *M*, 20 % H_2O_2 solution (0.11 *M*); the arrows indicate the moments of the addition of new portions of H_2O_2 (*1*); the same curves in the absence of PCA (*1′*); [PCA] = $4\cdot10^{-4}$ *M*, 36 % H_2O_2 solution (0.2 *M*) (*2*).

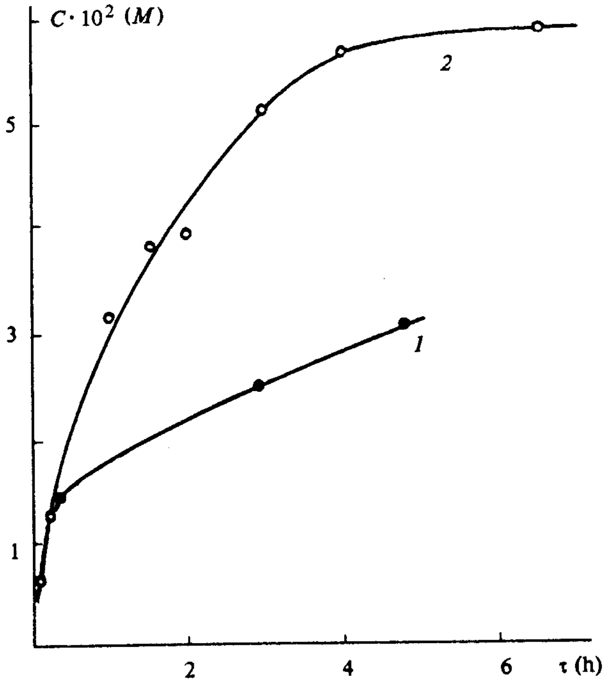

Fig. 3. Kinetic curves for benzaldehyde accumulation (*1*) upon the oxidation of benzyl alcohol (0.01 *M*) with hydrogen peroxide (0.11 *M*) and cyclohexanone accumulation (*2*) upon the oxidation of cyclohexanol (0.23 *M*) with hydrogen peroxide (0.2 *M*). MeCN was used as the solvent and $(Bu_4N)VO_3$ ($1\cdot10^{-4}$ *M*) and PCA ($4\cdot10^{-4}$ *M*) were the catalysts; the temperature was 50 °C.

lyst. Additional investigations are needed in order to reveal the mechanism of the process.

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