Oxidation by a H_2O_2—vanadium complex—2-pyrazinecarboxylic acid reagent

3.* Evidence for hydroxyl radical formation

G. V. Nizova and G. B. Shul'pin★

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

Evidence for the formation of hydroxyl radicals and their participation in hydrocarbon oxidation by a H_2O_2—vanadium complex—2-pyrazinecarboxylic acid reagent has been obtained by the spin trap method and kinetically, by competitive oxidation of a benzene—aliphatic alcohol mixture.

Key words: metallocomplex catalysis; oxidation; hydrogen peroxide; vanadium complexes; hydroxyl radicals.

Vanadium derivatives are efficient catalysts for the oxidation of organic compounds by hydrogen peroxide and alkyl peroxides.[2–11] Peroxide complexes of vanadium also stoichiometrically oxidize hydrocarbons.[12,13] The vanadate ion in combination with 2-pyrazinecarboxylic acid (PCA) catalyzes the oxidation, by hydrogen peroxide, of alkanes to alkyl peroxides, alcohols, and ketones,[14,15] of aromatic compounds to phenols,[1,14] and of alcohols to ketones or aldehydes.[1,14] It has been suggested that detachment of a hydrogen atom from the substrate by the hydroxyl radical that is generated during the interaction of a vanadium complex with H_2O_2, is the key stage of these processes. In the present work we attempted to verify the generation of these radicals and their participation in the oxidation.

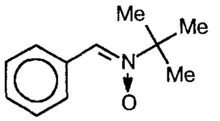
Experimental

Cyclohexane was oxidized according to the procedure described previously.[15] The reaction time was 0.5 h. An aliquot of the reaction solution (0.1 mL) was added to 0.4 mL of a 0.05 *M* solution of nitrone **1** in MeCN. The formation of the adduct of $OH^{\cdot}$ radicals with a spin trap was recorded on a Bruker E9 spectrometer at ~20 °C. Experimental conditions: modulation frequency was 100 kHz, modulation amplitude was 0.5 Oe, microwave power was 80 mW, frequency was 9.5 GHz.

Oxidation of the benzene—aliphatic alcohol mixture in acetonitrile was carried out in air in glass cylindrical vessels with a diameter of 20 mm kept at constant temperature by constant magnetic stirring. Concentrations of the initial reagents: benzene, 0.5 *M*; $(Bu_4N)VO_3$, $1 \cdot 10^{-4}$ *M*; PCA, $4 \cdot 10^{-4}$ *M*; and H_2O_2, $8.8 \cdot 10^{-2}$ *M*. Concentrations of MeOH, EtOH, and Pr^nOH for each series of competing reactions were 0.1, 0.2, 0.3, and 0.4 *M*. The total volume of the reaction solution was 5 mL. Phenol was isolated from an aliquot (0.2 mL) of the reaction solution by TLC on a Silufol UV-254 plate (eluent $CHCl_3$). The amount of phenol formed was determined spectrophotometrically by the absorption at λ = 274 nm. UV spectra were recorded on a Specord UV-VIS spectrophotometer.

Results and Discussion

The spin trap method is usually used for the fixation of radicals that arise in various processes (both in chemical processes and *in vivo*).[16–20] We used *N*-(benzilidene)-*tert*-butylamine *N*-oxide[16] (**1**) as such a trap. Adduct **2** was formed in the interaction of nitrone **1** with the $OH^{\cdot}$ radical.



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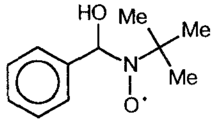

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A signal having a triplet structure with g = 2.0057±0.0002, a_N = 13.75 mT, and $a_H{}^{\beta}$ = 2.25 mT appears in the ESR spectrum of a solution containing the $(Bu_4N)VO_3$ complex ($1 \cdot 10^{-4}$ *M*), PCA ($4 \cdot 10^{-4}$ *M*), cyclohexane (0.46 *M*), and compound **1** (0.05 *M*) in acetonitrile after the addition of a 30 % aqueous solution of H_2O_2 (resulting concentration is 0.1 *M*). These parameters of the ESR spectrum agree satisfactorily with the corresponding values for the adduct of compound **1** with hydroxyl radicals formed in the photolysis of H_2O_2 in CH_3CN (g = 2.0054, a_N =

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* For part 2, see Ref. 1.

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15.5 mT, and a_{H}^{β} = 2.35 mT), and with the parameters for adduct **2** synthesized by the photolysis of H_2O_2 in an aqueous solution[16] (g = 2.0057, a_{N} = 15.3 mT, and a_{H}^{β} = 2.75 mT).

Some differences in the HFC parameters are likely to be caused by the interaction of adduct **2** and paramagnetic vanadium(IV) complexes. The lines in the spectrum of compound **2** formed in the system under study are much broader than those registered in the photolysis of H_2O_2 in acetonitrile. Since the concentration of adduct **2** is comparable to that of the vanadium complex, the decrease in a_{N} by ~10 % due to the interaction of two paramagnetic centers is quite reasonable in our opinion.

It should be mentioned that the ESR spectrum of adduct **2** is also registered during the interaction of a H_2O_2—vanadate system in MeCN with compound **1** in the absence of either cyclohexane or PCA. In the first case, this testifies that the adduct of compound **1** is not the product of the addition of the $C_6H_{11}OO^{\cdot}$ radical. On the other hand, hydroxyl radicals are likely generated by the vanadium complex in the absence of PCA as well, however, the concentration of these radicals is quite sufficient for detection by the sensitive spin trap method but is too small for the efficient oxidation of cyclohexane. It can be also that the vanadium complex decomposes H_2O_2 at a rate that is not less than in the presence of PCA but is rapidly transformed in the solution to an inactive particle.

We studied the kinetics of the competitive oxidation of benzene and various aliphatic alcohols in order to obtain additional information about the formation of hydroxyl radicals and their participation in the oxidation process. This method has been previously used successfully to prove the involvement of $OH^{\cdot}$ in oxidation by an ascorbic acid—Cu^{II}—oxygen system,[21] an ascorbic acid—ethylenediaminetetraacetic acid—Fe^{II}—oxygen (Udenfriend's system),[22] and Fe^{II}—H_2O_2 (Fenton's reagent).[22]

It was found that the rate of benzene oxidation decreases in the presence of aliphatic alcohols, which interact with hydroxyl radicals. As has been previously shown,[21] the ratio $[\mathrm{PhOH}]_0/[\mathrm{PhOH}]$ is proportional to $k_{\mathrm{A}}[\mathrm{AlkOH}]$ during the interaction of $OH^{\cdot}$ radicals with a benzene—aliphatic alcohol mixture, where $[\mathrm{PhOH}]_0$ and $[\mathrm{PhOH}]$ are phenol concentrations at a certain moment chosen in the initial part of the accumulation curve in the absence and presence of this alcohol, respectively, k_{A} is the rate constant for the interaction of the $OH^{\cdot}$ radical and this alcohol (*i.e.*, detachment of the hydrogen atom from the α-position of the alcohol molecule), and [AlkOH] is the concentration of the alcohol added. Thus, the existence of the linear correlation between $[\mathrm{PhOH}]_0/[\mathrm{PhOH}]$ and the constants k_{A} of several different alcohols attests to the participation of hydroxyl radicals in the key stage of this reaction. In the vanadium-containing system studied, the dependence of $[\mathrm{PhOH}]_0/[\mathrm{PhOH}]$ on alcohol concentration was determined for each of the following alcohols: methanol, ethanol, and 1-propanol. This dependence was linear for these alcohols, and the relationship $k_{\mathrm{A}}/k_{\mathrm{B}}$ was calculated from the slope of the line, where k_{A} and k_{B} are the rate constants for the oxidation of alcohol and benzene. As can be seen from Fig. 1, a satisfactory linear dependence between the values $k_{\mathrm{A}}/k_{\mathrm{B}}$ found experimentally by this method and the constants k_{A} known from literature[22] is observed. As has been already mentioned, the existence of this dependence confirms the participation of hydroxyl radicals in the oxidation by the H_2O_2—vanadium complex—PCA reagent.

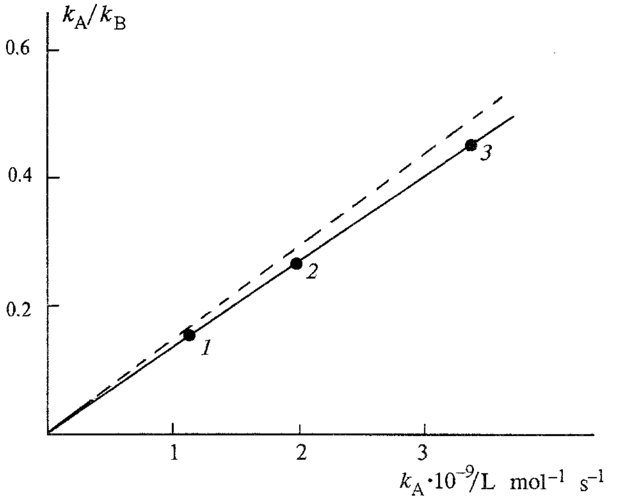
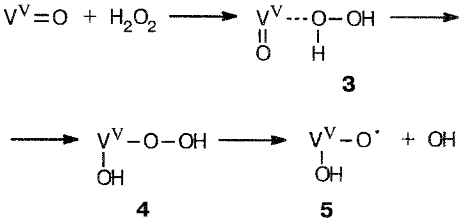


Fig. 1. Dependence of $k_{\mathrm{A}}/k_{\mathrm{B}}$ on k_{A} for the reaction of the competitive oxidation of the benzene and methanol mixture (*1*), ethanol (*2*), or 1-propanol (*3*) by a H_2O_2—VO_3^-—PCA system. The theoretical dependence[22] at k_{B} = 6.2 · 10^9 L mol^{-1} s^{-1} is presented by the dotted line.

Thus, the spin trap experiments provide evidence for the formation of hydroxyl radicals during oxidation by the H_2O_2—vanadium complex—PCA reagent, and kinetic data on the competitive oxidation of benzene—aliphatic alcohol mixtures confirm the supposition that these radicals participate in the key stage of the oxidation. The following stages, which result in the formation of hydroxyl radicals from H_2O_2, may be conceived. The coordination of H_2O_2 with the vanadium(V) oxocomplex results in the formation of adduct **3**, which is rearranged to the peroxide hydroxy derivative **4** (see Ref. 12), which then decomposes to generate hydroxyl radicals. The future of the remaining vanadium-containing radical-like particle **5** is unclear.



$$V^{V}{=}O + H_2O_2 \longrightarrow \underset{\mathbf{3}}{\underset{O}{\underset{\|}{V^{V}}}\cdots\underset{H}{\underset{|}{O}}{-}OH} \longrightarrow \underset{\mathbf{4}}{\underset{OH}{\underset{|}{V^{V}}}{-}O{-}OH} \longrightarrow \underset{\mathbf{5}}{\underset{OH}{\underset{|}{V^{V}}}{-}O^{\cdot}} + OH^{\cdot}$$

The role of PCA also remains unclear. The oxidation of cyclohexane and benzene in the absence of PCA occurs with a negligible yield. It is interesting that no increase in the concentration of the oxidation products is observed when PCA ($4 \cdot 10^{-4}$ *M*) and a new portion of H_2O_2 (resulting concentration is 0.4 *M*) is added to the solution formed after the oxidation of cyclohexane (0.46 *M*) by hydrogen peroxide (0.22 *M*) for 1 h at 40 °C in the presence of $(Bu_4N)VO_3$ ($1.1 \cdot 10^{-4}$ *M*) (the solution contains the products in a total concentration of $0.3 \cdot 10^{-5}$ *M*). This indicates that although the vanadium complex decomposes H_2O_2 in the absence of PCA to generate hydroxyl radicals, it is finally converted to a form that cannot be transformed into a catalytically active particle by the addition of PCA. It is obvious that an additional investigation is needed for the elucidation of the mechanism of the generation of $OH^{\cdot}$ radicals by the reagent described and of the role of PCA.

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