

Oxidation with the "O₂—H₂O₂—vanadium complex— pyrazine-2-carboxylic acid" reagent

11.* Oxidation of styrene, phenylacetylene, and their derivatives with the formation of benzaldehyde and benzoic acid

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The vanadium complex—pyrazine-2-carboxylic acid (PCA) system catalyzes oxidation of styrenes PhRC=CHR' (R = H, Me; R' = H, Ph) or phenylacetylenes PhC≡CR (R = H, Ph) with hydrogen peroxide in air to give aldehydes, ketones, and carboxylic acids. The reaction begins with H₂O₂ coordination to the vanadium ion followed by the formation of hydroxyl radicals. Catalytic action of PCA facilitates the reduction of the V^V complex to the V^{IV} complex and/or the stage of the formation of a peroxide derivative of vanadium.

Key words: olefins, styrene, phenylacetylene, oxidation, oxygenation, oxygen, hydrogen peroxide, metal complex catalysis, vanadium complexes, aldehydes, benzaldehyde, acetophenone, carboxylic acids, benzoic acid.

Previously,^{1–12} we showed that the vanadate ion in the presence of pyrazine-2-carboxylic acid (PCA) efficiently catalyzes oxidation of saturated hydrocarbons with hydrogen peroxide in acetonitrile or water in air with the predominant formation of alkyl hydroperoxides that slowly decompose in the course of reaction to yield the corresponding ketones (aldehydes) and alcohols. Experiments with labeled molecular oxygen showed that it is atmospheric oxygen that is the source of oxygen atoms in the molecule of the reaction product, whereas hydrogen peroxide acts as a promoter of the oxygenation. Aromatic hydrocarbons are oxidized with the formation of phenols, though the yields are relatively low. The main product of cyclohexene oxidation has the hydroperoxide substituent in the allyl position.

It was of interest to study the possibility of oxidation with the reagent discussed of other hydrocarbons containing, in particular, multiple bonds. In this work, styrene and phenylacetylene, as well as several of their derivatives, were chosen as oxidation substrates. It should be noted that the catalyzed oxidation of arylalkenes in air, resulting in the formation of carbonyl compounds, is well known (see, *e.g.*, Refs. 13–15).

Experimental

Oxidation of unsaturated hydrocarbons was carried out in air in a thermostatted cylindrical glass vessel with intense stirring. The volumes of the reaction solutions were 10 or 20 mL. Usually, an aliquot of a 35% aqueous solution of hydrogen peroxide was added to a solution of the catalyst (0.1 mmol L⁻¹ of vanadium complex and four-fold amount of PCA) and oxidizing substrate in MeCN. The conditions of particular experiments are given in the note to Table 1 and in the legends to the figures.

Table 1. Dependences of concentrations of benzaldehyde ([1]/mmol L⁻¹) and benzoic acid ([2]/mmol L⁻¹) formed in the oxidation of phenylacetylene on the initial concentration of hydrogen peroxide^a

[H ₂ O ₂] ₀ /mol L ⁻¹	25 h ^b		50 h ^b		290 h ^b	
	[1]	[2]	[1]	[2]	[1]	[2]
0.1	0.35	1.2	0.40	2.9	1.20	7.0
0.2	0.40	2.0	0.50	3.0	1.70	7.9
0.3	0.45	2.5	0.80	5.0	1.70	8.4
0.4	0.52	2.6	1.60	7.6	1.72	17.3
0.8	1.20	5.0	1.70	8.7	1.90	24.2

^a Reaction conditions: [HC≡CPh] = 0.2 mol L⁻¹, [VO(acac)₂] = 0.1 mmol L⁻¹, [PCA] = 0.4 mmol L⁻¹, MeCN, T = 23 °C.

^b Duration of the reaction.

* For Part 10, see Ref. 1.

The Bu^nNVO_3 salt was synthesized from V_2O_5 and Bu^n_4NOH following the procedure described earlier.¹⁶ A solution of the catalyst ($\text{NH}_4\text{VO}_3 + 4 \text{ PCA}$) was prepared by stirring a suspension of NH_4VO_3 (2.9 mg) and PCA (12.5 mg) in 100 mL of MeCN on slight heating. The pale-colored solution obtained (4 mL) was used for the preparation of 10 mL of the reaction solution. Phenylolefins and phenylacetylenes used as substrates were purified immediately prior to use by passing through a layer of silica gel.

The reaction mixture was analyzed by GLC (after addition of excess solid triphenylphosphine in order to reduce the unreacted H_2O_2) using a Philips PYE UNICAM PU 4500 chromatograph equipped with a flame-ionization detector with an Alltech ECONO-CAP Carbowax capillary column (30 m \times 0.25 mm; 0.25 μm) and a Shimadzu GC-17A chromatograph equipped with a flame-ionization detector with a capillary column (50 m \times 1 mm) and SE-52 as stationary phase. Helium was used as carrier gas. Quantitative analysis was performed after calibrating the chromatograms using solutions of the products with known concentrations. Formaldehyde that formed was determined following the procedure described previously.^{17,18}

Results and Discussion

We found that the reaction of styrene with hydrogen peroxide in acetonitrile in air, catalyzed by the $\text{Bu}^n_4\text{NVO}_3 + 4 \text{ PCA}$ system at 50–60 °C, results in the formation of benzaldehyde as the main product determined by GLC. The curves of styrene consumption and benzaldehyde accumulation as functions of time are shown in Fig. 1, from which it follows that the consumption of styrene is much higher than the amount of benzaldehyde accumulated in the system. This can be associated with the formation of side products, most of which have high molecular weights and cannot be determined by GLC. However, it should be noted that benzoic acid is formed only in low concentration under the given conditions. From comparing the curves shown in Fig. 1, *b* and *c* it follows that PCA is an essential component of the catalytic system and in the absence of PCA the reaction proceeds at a lower rate, though in this case the difference in the reaction rates is much less pronounced than the corresponding difference observed in the oxidation of saturated hydrocarbons.

In the preceding works of this series we used $\text{Bu}^n_4\text{NVO}_3$, which can be readily obtained¹⁶ from V_2O_5 and Bu^n_4NOH , as the vanadium-containing component of the catalytic system. However, it was of interest to study the possibility of using catalysts based on other vanadium derivatives. We found that an efficient catalytic system can be prepared in the form of an initial solution containing the vanadate ion by mixing NH_4VO_3 salt (it is insoluble in acetonitrile) and PCA. The kinetics of benzaldehyde accumulation in the oxidation of styrene catalyzed by this system is shown in Fig. 2. As can be seen, in this case the yield of benzaldehyde is even somewhat higher than in the oxidation catalyzed by the $\text{Bu}^n_4\text{NVO}_3 + 4 \text{ PCA}$ system. The system based on NH_4VO_3 also catalyzes the oxidation of *trans*-stilbene (0.2 mol L^{-1} , $[\text{H}_2\text{O}_2] = 0.8 \text{ mol L}^{-1}$, $[\text{NH}_4\text{VO}_3] =$

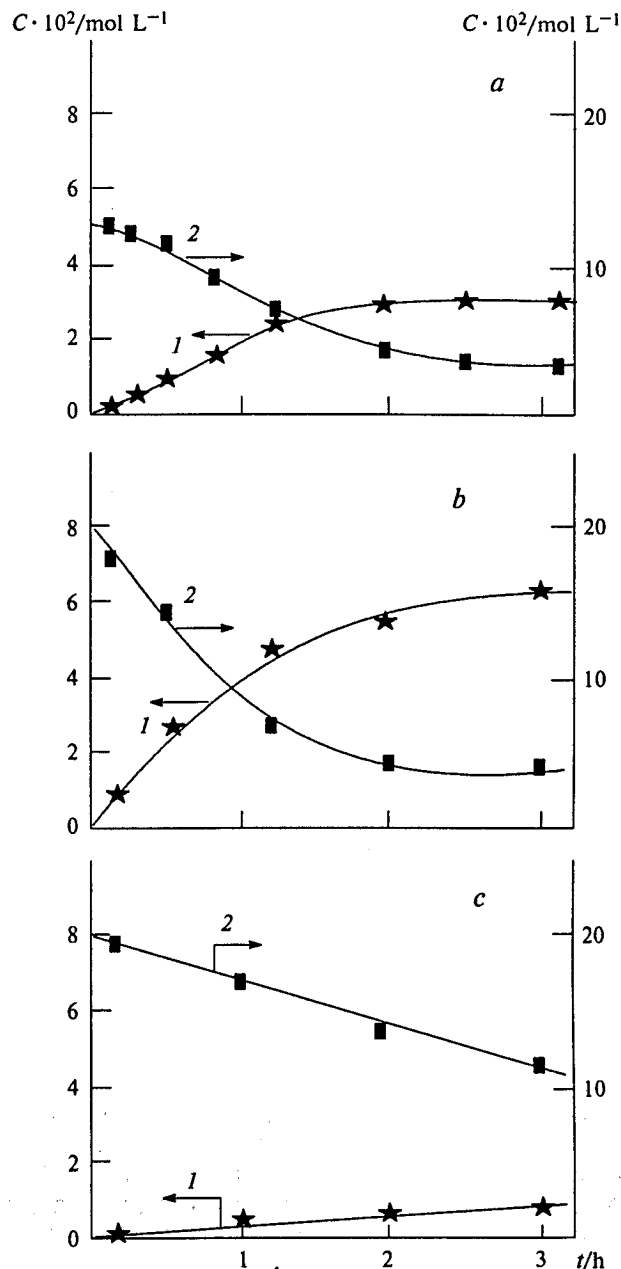


Fig. 1. Accumulation of benzaldehyde (1) and consumption of styrene (2) in the oxidation of styrene with atmospheric oxygen and H_2O_2 , catalyzed by $\text{Bu}^n_4\text{NVO}_3$ and PCA (*a*, *b*) and in the absence of PCA (*c*): *a*, $[\text{H}_2\text{O}_2] = 0.4 \text{ mol L}^{-1}$, $[\text{Bu}^n_4\text{NVO}_3] = 0.1 \text{ mmol L}^{-1}$, $[\text{PCA}] = 0.4 \text{ mmol L}^{-1}$, $T = 50 \text{ }^\circ\text{C}$; *b*, $[\text{H}_2\text{O}_2] = 0.8 \text{ mol L}^{-1}$, $[\text{Bu}^n_4\text{NVO}_3]$ and $[\text{PCA}]$ are the same as in Fig. 1, *a*, $T = 60 \text{ }^\circ\text{C}$; and *c*, $[\text{H}_2\text{O}_2] = 0.8 \text{ mol L}^{-1}$, $T = 60 \text{ }^\circ\text{C}$.

0.1 mmol L^{-1} , $[\text{PCA}] = 0.4 \text{ mmol L}^{-1}$, MeCN, $T = 60 \text{ }^\circ\text{C}$) to give benzaldehyde.

<i>t</i> /min	$[\text{PhC(O)H}]$ /mmol L^{-1}	<i>t</i> /min	$[\text{PhC(O)H}]$ /mmol L^{-1}
5	8.4	60	110
20	56	120	150

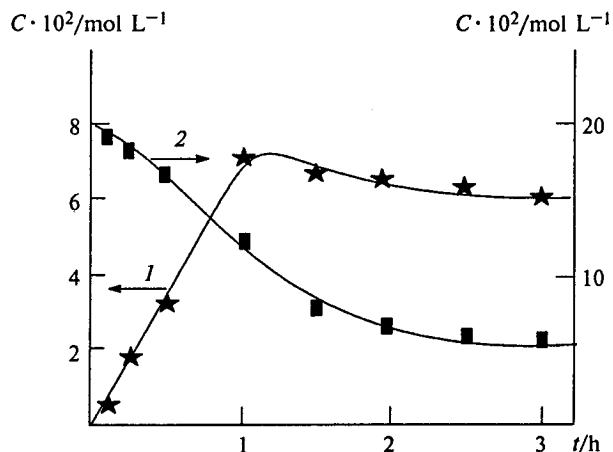


Fig. 2. Accumulation of benzaldehyde (1) and consumption of styrene (2) in the oxidation of styrene (0.2 mol L^{-1}) with atmospheric oxygen and H_2O_2 (0.8 mol L^{-1}), catalyzed by NH_4VO_3 (0.1 mmol L^{-1}) and PCA (0.4 mmol L^{-1}) (the reagent was prepared preliminarily, see Experimental), $T = 60^\circ\text{C}$.

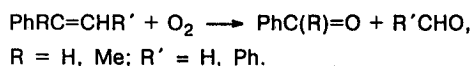
Thus, in this case the yield of benzaldehyde amounts to 75% with respect to *trans*-stilbene.

Oxidation of α -methylstyrene (0.2 mol L^{-1}) and α -methyl-*trans*-stilbene (0.1 mol L^{-1}) with hydrogen peroxide (0.4 and 0.2 mol L^{-1} , respectively) was carried out using the $\text{VO}(\text{acac})_2 + 4 \text{ PCA}$ system as catalyst. The yields of the products (their concentrations are given in parentheses) in the absence of PCA are approximately halved.

Substrate	$T/^\circ\text{C}$	t/h	$[\text{PhC(O)H}]$ mmol L^{-1}	$[\text{MeC(O)Ph}]$ mmol L^{-1}
α -Methylstyrene	60	2	—	41 (20)
	23	170	—	81 (40)
α -Methyl- <i>trans</i> -stilbene	23	120	8.1 (5.0)	11 (7)

Similarly to the unsubstituted styrene, α -methylstyrene is oxidized to give formaldehyde as the second product, which was qualitatively proved using the Nash reagent.¹⁷

Thus, oxygenation of olefins $\text{PhRC}=\text{CHR}'$ in the general case proceeds by the following equation:



The $\text{VO}(\text{acac})_2 + 4 \text{ PCA}$ system also catalyzes the oxidation of phenylacetylene. It is noteworthy that the concentration of benzaldehyde (1) that formed in this reaction at high temperature (60°C) is only slightly lower than that of benzoic acid (2); however, acid 2 becomes the main reaction product (Fig. 3, see Table 1) at room temperature, especially when using large amounts of hydrogen peroxide. For instance, the [2] : [1] ratio amounts to 13 : 1 after 290 h at $[\text{H}_2\text{O}_2]_0 = 0.8 \text{ mol L}^{-1}$

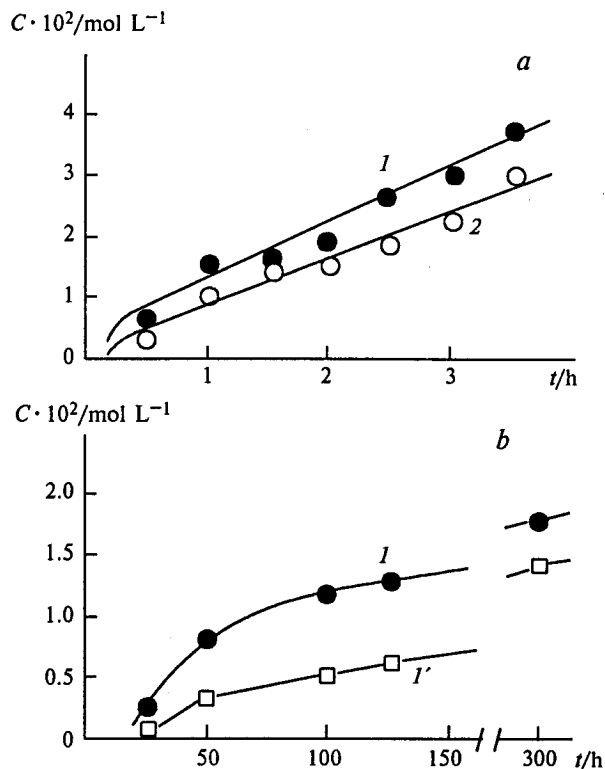


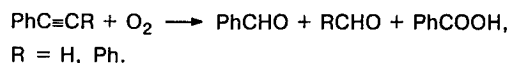
Fig. 3. Accumulation of benzoic acid (1, 1') and benzaldehyde (2) in the oxidation of phenylacetylene with atmospheric oxygen and H_2O_2 (0.4 mol L^{-1}), catalyzed by $\text{VO}(\text{acac})_2$ (0.1 mmol L^{-1}) and PCA (0.4 mmol L^{-1}) (1, 2) and in the absence of PCA (1'): a, $[\text{HC}=\text{CPh}] = 0.4 \text{ mol L}^{-1}$, $T = 60^\circ\text{C}$; and b, $[\text{HC}=\text{CPh}] = 0.2 \text{ mol L}^{-1}$, $T = 23^\circ\text{C}$.

and $T = 23^\circ\text{C}$. The predominant formation of acid 2 instead of aldehyde 1 distinguishes the reaction of phenylacetylene oxidation from the oxidation of styrene. The second characteristic feature of the reaction with participation of phenylacetylene is a relatively small acceleration of the reaction caused by the introduction of PCA (see Fig. 3, b) at room temperature, whereas the oxidation rates at 60°C are virtually equal in the presence and in the absence of PCA. The reaction proceeds with an induction period.

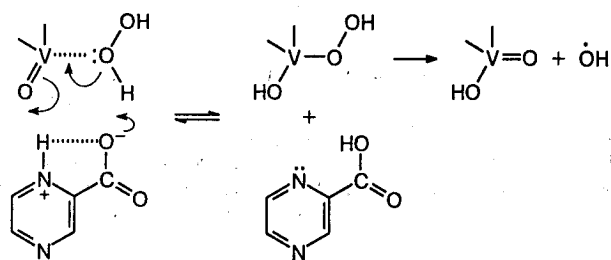
Oxidation of tolan (0.2 mmol L^{-1}) with atmospheric oxygen and hydrogen peroxide (0.4 mmol L^{-1}) catalyzed by the $\text{VO}(\text{acac})_2 + 4 \text{ PCA}$ (0.1 and 0.4 mmol L^{-1} , respectively) system in acetonitrile also results in the formation of acid 2 as the main product, though in a low yield, whereas the addition of PCA causes only a slight acceleration of the reaction (the concentrations of the products obtained in the absence of PCA are given in parentheses).

$T/^\circ\text{C}$	t/h	$[\text{PhC(O)H}]$ mmol L^{-1}	$[\text{PhCOOH}]$ mmol L^{-1}
60	2	1.2	2.0
23	300	0.35 (0.25)	3.5 (3.1)

Thus, the reaction with acetylene hydrocarbons, in the general case, follows the equation



Oxidation of styrene, phenylacetylene, and their derivatives under the conditions described above most likely follows a radical mechanism. In the first stage, the vanadium derivative reacts with hydrogen peroxide to generate hydroxyl radicals. One of the possible reaction routes can be⁸ the reduction of V^V to V^{IV} by the first H₂O₂ molecule. In this case the role of PCA, which is an electron donor (or reservoir), consists in facilitation of this process (PCA acts as an analog of the porphyrin ligand in biological and biomimetic oxidation on metal-porphyrin complexes of transition metals). In fact, on going from hardly oxidizable alkanes to olefins and, especially, to acetylenes, the rates of oxidation reactions in the presence and in the absence of PCA approach each other (phenylacetylene is a sufficiently good electron donor to be used instead of PCA). Reaction of V^{IV} with the second H₂O₂ molecule results in the formation of a hydroxyl radical that attacks the molecule of the unsaturated hydrocarbon.^{19,20} Then, the reaction can occur as a chain process involving atmospheric oxygen. Catalytic action of PCA in the oxidation can also be explained by suggesting its participation in the proton transfer from the hydrogen peroxide molecule coordinated to the vanadium ion to the oxo ligand of the complex. This results in the formation of a peroxide-vanadium complex, which then decomposes releasing a hydroxyl radical. PCA can play its role in the form of a zwitterion in the act of proton transfer (formal redistribution of ordinary bonds is shown by arrows).



In conclusion it may be said that, despite the fact that the oxidation of phenyl-containing unsaturated hydrocarbons with atmospheric oxygen and hydrogen peroxide catalyzed by the vanadium complex-PCA system results in the formation of oxygenation products (aldehydes, ketones, and carboxylic acids) in low yields, this reaction is of interest since its peculiarities are in agreement with the assumption of the generation of hydroxyl radicals in the system under study and do not contradict the hypothesis for the role of PCA as an electron donor facilitating the reduction of vanadium complex in one of the initial reaction stages.

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