

**PHOTOCHEMICAL OXIDATION OF HYDROCARBONS BY A  
VANADIUM(V) PEROXO COMPLEX**

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*The oxidation of alkanes and benzene by  $VO(O_2)L \cdot 2H_2O$  ( $L = 2$ -picolinate) in acetonitrile is accelerated upon irradiation with visible and, especially, UV light. Cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone in approximately 2:1:1 ratio are formed from cyclohexane both in the dark and photochemical reactions. Benzene is oxidized to phenol.*

**Keywords:** oxidation, hydrocarbons, photochemistry, peroxo complexes, and vanadium.

The photochemical oxidation of hydrocarbons involving transition metal complexes [1-3] holds considerable interest since they may provide for the selective conversion of hydrocarbon raw materials under mild conditions. There have been recent studies of photochemical, stoichiometric [4-6], and catalytic reactions of oxo complexes with hydrocarbons [7-14], leading to oxidation of the hydrocarbons. On the other hand, the reactions of transition metal peroxo complexes proceeding upon irradiation have not been studied extensively [15, 16].

In the present work, we were the first to study the effect of irradiation on the oxidation of saturated and aromatic hydrocarbons by a peroxo complex.  $VO(O_2)L \cdot 2H_2O$ , where  $L = 2$ -picolinate, obtained previously by Mimoun et al. [17], was used as such an oxidizing agent. We should note that this peroxo complex in acetonitrile oxidizes hydrocarbons at a significant rate at room temperature even in the dark [17-19].

In a study of the dark reaction with cyclohexane (1), we found that the ratio of the products, cyclohexanol (2) and cyclohexanone (3), varies significantly depending on whether triphenylphosphine is added to the reaction solution prior to the gas-liquid chromatographic analysis. Without prior reduction by  $PPh_3$ , alcohol 2 and ketone 3 are formed in approximately equal amounts. Thus, the reaction of 0.02 M complex with 0.23 M 1 at 20°C over 1.5 h gives  $3.9 \cdot 10^{-3}$  M 2 and  $3.7 \cdot 10^{-3}$  M 3. After reduction, the concentration of 2 increases to  $6.1 \cdot 10^{-3}$  M due to a decrease in the concentration of 3 to  $1.7 \cdot 10^{-3}$  M. Such a change apparently results from the reaction of  $PPh_3$  with initially formed cyclohexyl hydroperoxide (4), which, in the absence of a reducing agent, decomposes upon chromatography to give the alcohol and ketone in approximately equal amounts.<sup>†</sup> The decomposition and reduction of the peroxide were studied in detail by Galimova et al. [20].

We note that, in the case of unreduced phosphine, the change in the 2/3 ratio cannot be significantly due to the oxidation of 1 by the peroxo complex in the reaction solution in the injector or chromatograph column. Indeed, at the onset of the reaction when the concentration of the peroxo complex is high, only small amounts of 2 and 3 are found in the gas-liquid chromatographic analysis of the unreduced solution. These results indicate that the dark reaction of  $VO(O_2)L \cdot 2H_2O$  with 1 leads to the formation of 2, 3, and 4 in approximately 1:1:2 ratio. The oxidation of 1 occurs with an induction period (Fig. 1). The induction period is reduced upon irradiation of the orange solution with visible light. In this case, the yield of the oxidation products increases somewhat (see scheme below).

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†The analysis was carried out on a Perkin-Elmer 8500 chromatograph using 2-m steel columns packed with 5% Carbowax on Chromosorb W80/100 and helium as the gas carrier with a HP 3390A integrator.

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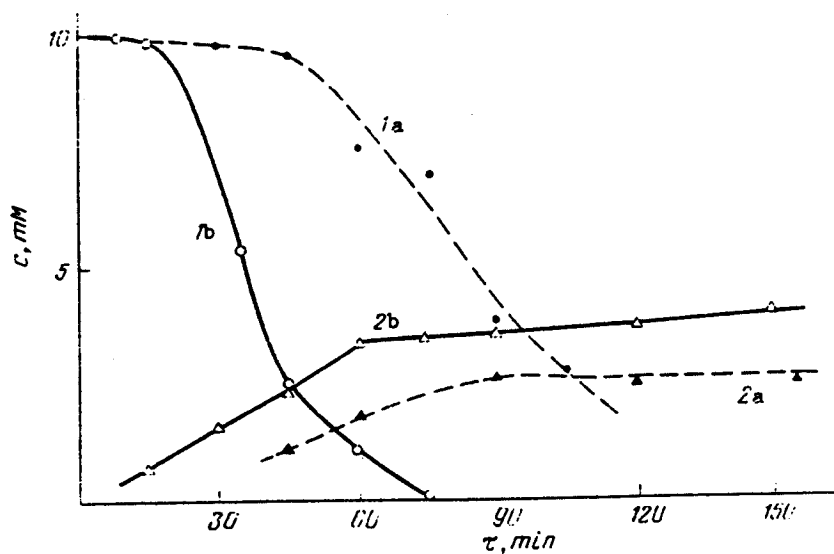


Fig. 1. Kinetics for the decomposition of  $\text{VO}(\text{O}_2)\text{L}\cdot 2\text{H}_2\text{O}$  (1) and accumulation of the sum of the oxygenation products of 0.232 M cyclohexane (2) in the dark (a) and upon irradiation (b) at 20°C using 100-W incandescent lamp.

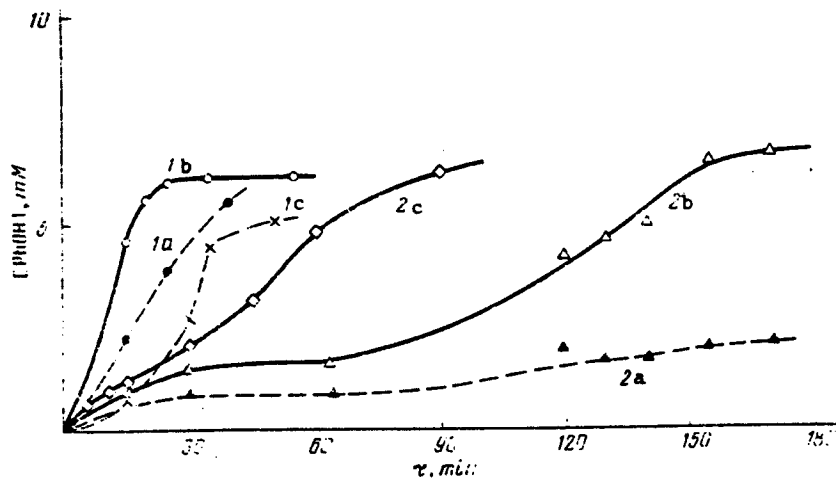
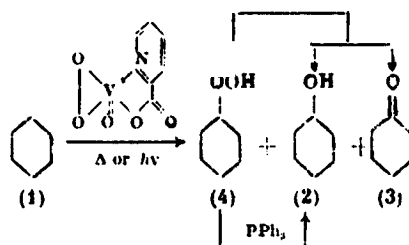


Fig. 2. Kinetics of phenol accumulation in the oxidation of 1.12 M benzene by 0.02 M  $\text{VO}(\text{O}_2)\text{L}\cdot 2\text{H}_2\text{O}$  in acetonitrile in the dark (a) upon irradiation by the full light of a 100-W incandescent lamp (b), and irradiation by a medium-pressure mercury lamp ( $\lambda > 300$  nm) (c). Solution temperature: 20°C (1) and 3°C (2). 1c) experiment with additive of 0.005 M 2,6-di(*tert*-butyl)-4-methylphenol.



The accelerating effect of light in the case of the hydroxylation of benzene at room temperature is even more evident (Fig. 2). Irradiation with UV light is even more efficient. The shape of the kinetic curves for the accumulation of phenol at 3°C shows that the reaction proceeds by a complex, multistep mechanism, which apparently is unchanged upon going from the dark reaction to the photochemical process.

We have also found that the selectivity parameters in the oxidation of alkanes in the dark and photochemical reaction are similar. Thus, the 1°:2°:3° selectivity (the relative reactivity of a C–H bond at primary, secondary, and tertiary carbon atoms) for the oxidation of 3-methylhexane is 1:7:90 for the dark reaction and 1:6:80 for the photochemical reaction. The determination of the  $\Psi$  parameter [21], which characterizes the reactivity of the CH<sub>2</sub> group in ethylbenzene relative to that in cyclohexane, gave values of 1.6 for the dark reaction and 1.8 for the photochemical process. The reaction may begin with opening of the peroxide ring in the vanadium complex [17] and is accompanied by the formation of various radical-like species, including HO· radicals, which, upon reacting with the starting peroxy complex, convert it into a reactive state. Indeed, the addition of a slight amount of 2,6-di(*tert*-butyl)-4-methylphenol leads to a marked increase in the induction period in the formation of phenol (Fig. 2).

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