

LETTERS TO THE EDITOR

OXIDATION OF ALKANES BY PEROXIDE COMPLEXES OF
PALLADIUMJ. Muzart,* G. V. Nizova, A. Riahi,*
and G. B. Shul'pin

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In spite of the fact that the peroxide derivatives of transition metals are intermediate compounds in a series of oxidation processes [1-4] only a few examples of the oxidation of hydrocarbons by individual peroxide complexes are known [5-8]. In the present work we investigated the possibility of oxidation of alkanes by metal peroxides not only under thermal conditions but also under the influence of light. We found that when a solution of $[(t\text{-BuOO})\text{Pd}(\text{OCOCH}_3)]_2$ (I) [9] ($2.3 \cdot 10^{-3}$ M) and cyclohexane (II) (0.92 M) in methylene chloride (previously distilled in an atmosphere of argon) was exposed to the total light of a high-pressure mercury lamp in a glass vessel ($\lambda > 310$ nm, 15°C) for 3 h $2.7 \cdot 10^{-4}$ M of cyclohexanol (III) and $1.8 \cdot 10^{-4}$ M of cyclohexanone (IV) were formed. Exposure of a solution of compound (II) in benzene in the presence of the peroxide (I) ($1.2 \cdot 10^{-4}$ M) under similar conditions in air for 0.5 h gave $1.3 \cdot 10^{-3}$ M of compound (III) and $1.0 \cdot 10^{-3}$ M of the derivative (IV). In the presence of $[(t\text{-BuOO})\text{Pd}(\text{OCOCF}_3)]_2$ (V) under the same conditions $1.4 \cdot 10^{-3}$ M of compound (III) and $1.2 \cdot 10^{-3}$ M of compound (IV) were formed. Thus, in this case the yield of the oxidation products amounted to five molecules to one palladium atom. It is important to note that cyclohexyl hydroperoxide (VI) and phenol were not detected in the reaction mixture during exposure in air. In contrast to the previously described photooxidation of alkanes in the presence of metal chlorides [2], in the present case the catalytic action of the palladium complex cannot be due to intermediate formation of the chlorine radical.

Other alkanes can also be oxidized with photocatalysis by palladium complexes. The selectivity (the relative reactivity of the C—H bonds at the primary 1° , secondary 2° , and tertiary 3° carbon atoms) for the photooxidation of 3-methylhexane amounted to $1^\circ:2^\circ \geq 1:10$ and $3^\circ:2^\circ \approx 30$.

In the dark reaction of the hydrocarbon (II) (0.92 M) with the peroxide (V) ($5.0 \cdot 10^{-3}$ M) in benzene after 24 h in argon at 20°C $1.1 \cdot 10^{-3}$ M of compound (III) and $0.9 \cdot 10^{-3}$ M of the ketone (IV) were formed, and $0.6 \cdot 10^{-3}$ M of the hydroperoxide (VI) was also obtained. The selectivity in the oxidation of 3-methylhexane $1^\circ:2^\circ:3^\circ \approx 1:10:400$. (The formation of a significant amount of isomeric alkyl hydroperoxides was also detected in this reaction.)

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*Jacques Muzart and Abdelkhalik Riahi, Université de Reims Champagne-Ardenne, Faculté des Sciences, Associée au C.N.R.S., 51062 Reims Cedex, France.

University of Reims, Champagne-Ardenne, National Center of Scientific Research, France. N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow. Translated from *Zhurnal Obshchei Khimii*, Vol. 62, No. 5, pp. 1177-1178, May, 1992. Original article submitted June 19, 1991.