

PHOTOOXIDATION OF ALKANES AND BENZENE BY POLYVANADATE IN  $\text{CF}_3\text{CO}_2\text{H}$ 

M. M. Kats and G. B. Shul'pin

UDC 542.943:541.141.7:546.881-128:547.  
464.2'161:547.592.1:547.216

Despite the significant interest in the activation of the C-H bond in alkanes by metals in a high oxidation state [1], only a few examples have been reported for the stoichiometric photooxidation of alkanes by oxo complexes (Cr [2,3], Ru and Os [4], and W [5]). We have found that the irradiation of a solution of the polyvanadate ion by the full light of a 125-W incandescent lamp in anhydrous  $\text{CF}_3\text{CO}_2\text{H}$  in the presence of an alkane gave oxidation of the alkane. The total volume of the reaction solution was 10 ml. The concentration of  $\text{KVO}_3$  was 0.02 mole/liter. Dissolution was carried out over 72 h. Thus, the irradiation of 0.46 mole/liter cyclohexane over 8 h gave  $5.5 \cdot 10^{-3}$  mole/liter cyclohexyl trifluoroacetate and  $4.3 \cdot 10^{-3}$  mole/liter cyclohexanone. The irradiation of 0.38 mole/liter hexane over 3 h gave trifluoroacetates derived from isomeric hexanols as well as carbonyl compounds. The treatment of this product mixture with  $\text{NaBH}_4$  in methanol gave a mixture of  $0.37 \cdot 10^{-3}$  mole/liter 3-hexanol,  $1.10 \cdot 10^{-3}$  mole/liter 2-hexanol, and  $0.24 \cdot 10^{-3}$  mole/liter 1-hexanol. Thus, the relative reactivity per hydrogen atom at  $\text{C}^3$ ,  $\text{C}^2$ , and  $\text{C}^1$  in hexane is 1:2.9:0.43. Benzene (0.56 mole/liter) rapidly reduces  $\text{V}^{5+}$  upon irradiation for 1 h to give a mixture of organic products, including phenyl trifluoroacetate isolated at phenol ( $0.26 \cdot 10^{-3}$  mole/liter). The reaction with alkanes and benzene virtually does not proceed in the absence of light. For example, the reduction of  $\text{V}^{5+}$  by hexane is not detected even after heating at  $60^\circ\text{C}$  for 8 h. On the other hand, ethylbenzene and toluene are rapidly oxidized in a dark reaction at  $10^\circ\text{C}$ .

## LITERATURE CITED

1. A. E. Shilov and G. B. Shul'pin, *Usp. Khim.*, 56, 754 (1987).
2. G. B. Shul'pin, P. Lederer, and E. Matsova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2638 (1986); G. V. Shul'pin, E. Matsova, and P. Lederer, *Zh. Obshch. Khim.*, 59, 2604 (1989).
3. G. B. Shul'pin, A. N. Druzhinina, and G. V. Nizova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 212 (1990).
4. V. W.-W. Yam and C.-M. Che, *New J. Chem.*, 13, 707 (1989).
5. N. Z. Muradov and M. I. Rustamov, *Dokl. Akad. Nauk SSSR*, 303, 656 (1988).