

CYCLOHEXANE PHOTOOXYGENATION BY AIR OXYGEN IN  $\text{CH}_2\text{Cl}_2$  IN THE PRESENCE OF CHROMIUM OXOCOMPLEX-IODOSYLBENZENE SYSTEM

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Cyclohexane is oxidized by air oxygen in  $\text{CH}_2\text{Cl}_2$  solution to yield cyclohexanol, cyclohexanone and cyclohexyl chloride when irradiated by light ( $\lambda > 310$  nm) in the presence of  $(\text{Bu}_4\text{N})_2\text{CrO}_4$  or  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$ . The addition of PhIO greatly accelerates the reaction and increases the yield of products. The reaction mixture contains neither cyclohexanol nor cyclohexanone when the photoreaction in the presence of the Cr(VI)-PhIO system is carried out in argon atmosphere. Hence neither iodosylbenzene nor oxochromium compounds can be oxygen atom donors in alkane oxygenation. The accelerating effect of iodosylbenzene may be due to the enhanced oxidizing power of photo-excited oxochromium species when coordinated to iodosylbenzene.

Циклогексан окисляется кислородом воздуха в растворе  $\text{CH}_2\text{Cl}_2$  с образованием циклогексанола, циклогексанона, а также циклогексилхлорида при облучении светом ( $\lambda > 310$  нм) в присутствии  $(\text{Bu}_4\text{N})_2\text{CrO}_4$  или  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$ . Добавка PhIO сильно ускоряет реакцию и увеличивает выходы продуктов. Когда реакция в присутствии системы Cr(VI)-PhIO проводилась в атмосфере аргона, в реакцион-

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ной смеси не были обнаружены ни циклогексанол, ни циклогексанон. Таким образом, иодозобензол (как и оксохромовое соединение) не являются донорами кислородного атома в реакции оксигенирования. Ускоряющее влияние иодозобензола может быть объяснено увеличением окисляющей способности фотовозбужденной оксохромовой частицы при ее координации с иодозобензолом.

Iodosylbenzene (PhIO) is known to oxygenate alkanes and olefins if transition metal complexes are used as catalysts [1-3]. Thus, the catalytic epoxidation of olefins with iodosylbenzene by a series of chromium(III) cations  $\text{Cr}(\text{salen})_5^+$  was promoted by pyridine N-oxide (pyO). Oxo chromium(V) derivatives  $\text{O}=\text{Cr}(\text{salen})^+$  and  $\text{O}=\text{Cr}(\text{salen})(\text{pyO})^+$  as reactive intermediates in the catalytic cycle were identified by spectral analysis and X-ray crystallography [4]. Oxo chromium(VI) compounds were shown to catalyze the oxygenation of alkanes and arylalkanes with PhIO at room temperature in dark reactions [5,6]. The rate of these reactions carried out in air-saturated solvents is very low. Apparently, air dioxygen takes part in oxygenation [5]. The main reaction route, however, can be assumed to involve a transfer of oxygen from PhIO to alkane through the oxochromium compound.

Here we present the results of studying cyclohexane oxygenation by oxochromium(VI) compounds with and without iodosylbenzene under light irradiation.

Oxygenation reactions were carried out in air in a Pyrex vessel with a water-cooled (16 °C) jacket under continuous stirring with a total of 5 mL of reaction solution. The source of irradiation was the full light of a street luminescent lamp (250 W). Products were analyzed using the GLC method.

$(\text{Bu}_4\text{N})_2\text{CrO}_4$  and  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$  compounds were used as oxidizing agents or catalysts. Methylene chloride was a solvent. The main products of the photochemical reaction were cyclohexa-

nol, cyclohexanone and small amounts of cyclohexyl chloride. The kinetics is illustrated in Figs 1 and 2. Both oxocompounds are easily soluble in  $\text{CH}_2\text{Cl}_2$ . Iodosylbenzene is not soluble during the initial period but then is gradually dissolved and after approximately 2-3 h of irradiation, the solution becomes homogeneous. It should be noted that in all cases neither cyclohexanol nor cyclohexanone were detected in the solution after 28 h of dark reaction. It can be seen that under irradiation (i)  $(\text{Bu}_4\text{N})_2\text{CrO}_4$  is a stronger oxidant than  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$ ; (ii) for both oxocompounds the yield of products is below 1 mol per mol of oxidant; (iii) the ketone/alcohol ratio is  $\geq 1$  in the case of a stronger oxidant; (iv) PhIO accelerates oxidation and

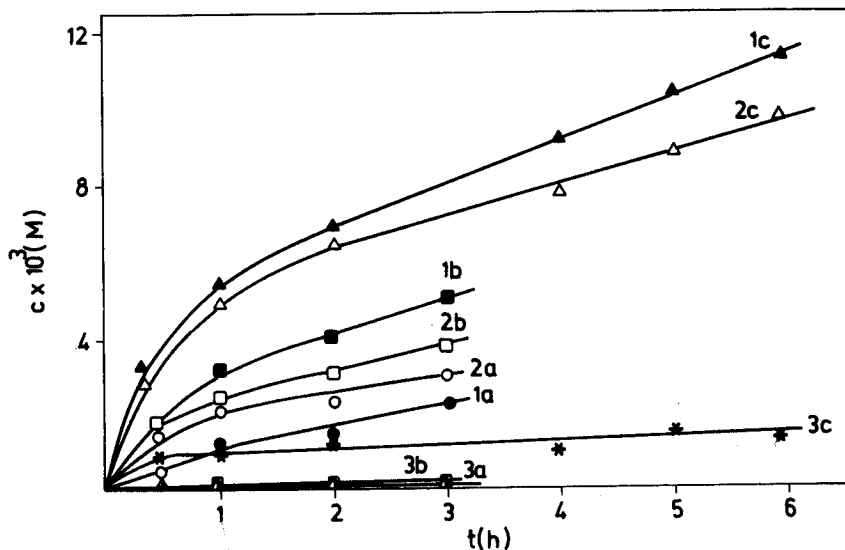


Fig. 1. Yield of cyclohexanol (1), cyclohexanone (2) and cyclohexyl chloride (3) in photooxygenation of cyclohexane (0.46 M) in air-saturated  $\text{CH}_2\text{Cl}_2$  in the presence of  $2 \times 10^{-3}$  M  $(\text{Bu}_4\text{N})_2\text{CrO}_4$  (a),  $2 \times 10^{-3}$  M  $(\text{Bu}_4\text{N})_2\text{CrO}_2$  and  $2 \times 10^{-5}$  mol PhIO (b) and  $2 \times 10^{-3}$  M  $(\text{Bu}_4\text{N})_2\text{CrO}_4$  and  $5 \times 10^{-5}$  mol PhIO (c)

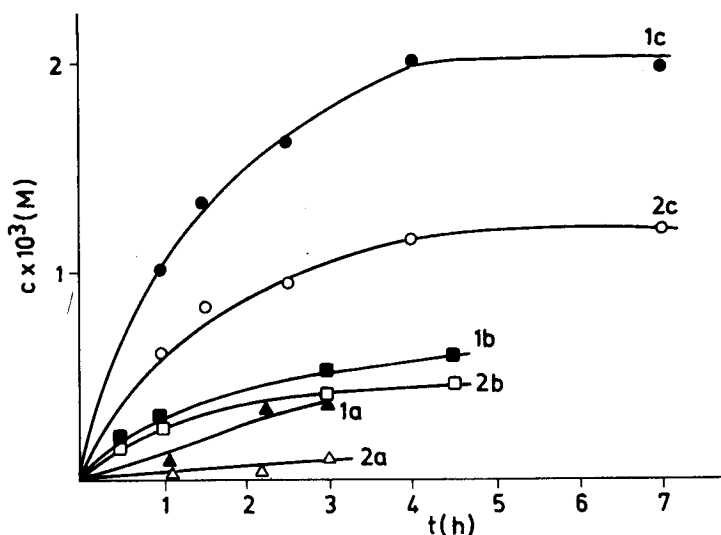


Fig. 2. Yield of cyclohexanol (1) and cyclohexanone (2) in photooxygenation of cyclohexane (0.46 M) in air-saturated  $\text{CH}_2\text{Cl}_2$  in the presence of  $1.0 \times 10^{-2}$  M  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$  (a),  $2 \times 10^{-3}$  M  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$  and  $2 \times 10^{-3}$  mol PhIO (b) and  $2 \times 10^{-3}$  M  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$  and  $5 \times 10^{-5}$  mol PhIO (c)

increases the yield of products in all cases; (v) reaction rates and yields grow with increasing amount of PhIO; (vi) the ketone/alcohol ratio is  $< 1$  in all cases when PhIO is added.

It should be noted that when the reactions are carried out in argon atmosphere, the concentrations of cyclohexanol and cyclohexanone after 4 h irradiation are below  $2 \times 10^{-4}$  M even at  $5 \times 10^{-5}$  M concentration of PhIO (with  $2 \times 10^{-3}$  M  $(\text{Bu}_4\text{N})_2\text{CrO}_4$  or  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$ ). In the absence of dioxygen iodosylbenzene is insoluble in  $\text{CH}_2\text{Cl}_2$ .

Thus it can be suggested that either in the presence or absence of iodosylbenzene the source of oxygen atoms in the oxochromium(VI)-induced photooxidation of cyclohexane is air dioxygen rather than an oxochromium compound or iodosylbenzene.

Apparently, the photoexcited oxochromium species detaches a hydrogen atom from alkane RH to generate radical R'. The latter rapidly reacts with dioxygen to produce a peroxide radical ROO', then yielding alcohol and ketone apparently capable of reoxidizing Cr(V)-OH to Cr(VI) = 0 [7]. Iodosylbenzene accelerates the photoreaction acting probably as an electrophilic reagent or Lewis acid. The reactivity of oxochromium(VI) compounds in oxidation reactions is known [8] to increase in the presence of protic acids, and iodosylbenzene was shown [9] to act as an electrophilic agent in interaction with olefins in the presence of metal compounds. In our case iodosylbenzene can be coordinated to oxochromium compound and increase the electrophilic properties of chromium oxidants. Coordination can be realized through the oxygen atom of chromium compounds and the iodine atom of iodosylbenzene (similar to protonation of the Cr=O bond) or through the oxygen atom of iodosylbenzene and the chromium atom of oxocomplexes. The electron-accepting effect of iodosylbenzene should increase the ability of the photoexcited oxochromium species to detach alkane hydrogen atoms. Indeed, when going from  $\text{CrO}_4^-$  to the more electron-rich complex  $(\text{Bu}_3\text{SnO})_2\text{CrO}_2$ , the photooxidizing power of oxochromium compounds decreases.

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