

PHOTO-OXYGENATION OF CYCLOHEXANE BY ATMOSPHERIC OXYGEN IN METHYLENE CHLORIDE, CATALYSED BY A Cr(IV) OXOCOMPLEX*†

J. MUZART,‡ A. N. DRUZHININA and G. B. SHUL'PIN

Reims University, Champagne-Ardenne, France
N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow

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During the visible light irradiation in air of a solution of cyclohexane and a complex of Cr(IV) with pyridinium $C_5H_5NHCrO_3Cl$ in CH_2Cl_2 , roughly equal quantities of cyclohexanol and cyclohexanone are formed (cyclohexylhydroperoxide is not found). A total of about eight molecules of the products per oxocomplex molecule are formed within 4 hr.

Chromium complexes are widely used as catalysts in the oxidation of different organic substances [2], including hydrocarbons. Earlier it was shown that chromium(VI) oxocompounds catalyse the oxygenation of saturated and alkylaromatic hydrocarbons by hydrogen peroxide [3, 4] and organic peroxides [5–8]. Furthermore, the photo-oxidation of these compounds by atmospheric oxygen in the presence of catalytic amounts of Cr(VI) has been described [9–13]. In the literature there are very little data on the use of an unusually stable Cr(IV) derivative, i.e. a complex with pyridinium $C_5H_5NHCrO_3Cl$, as the catalyst [14]. This complex catalyses the oxidation of methylene groups in the α -position by *tert*-butylhydroperoxide to an aryl, ethylene and acetylene fragment [15]. The reaction was carried out in CH_2Cl_2 at room temperature. It was of interest to establish the possibility of using a Cr(IV) oxocomplex in the photocatalytic oxidation of hydrocarbons.

EXPERIMENTAL

The reactions were carried out with stirring of the solution in air at $\sim 15^\circ C$ in cylindrical, 20 mm diameter glass vessels equipped with jackets cooled by running water. For irradiation, use was made of the full light of two filament lamps (2×200 W). The total volume of the solution was 5 ml. After certain time intervals, samples of the reaction solution were taken, and these were analysed twice by means of GLC — with direct injection into the chromatograph without preliminary treatment and after the addition of excess triphenylphosphine for 10–20 min with the aim of reducing cyclohexylhydroperoxide to cyclohexanol. Use was made of an LKHM-

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‡ Jacques Muzart, Université de Reims, Champagne-Ardenne, Faculté des Sciences, Associée au CNRS, B. P. 347, 51062 Reims Cédex, France.

80/6 chromatograph (column length 2 m, diameter 4 mm, sorbent INERTON AW-HMDS 315–320 μm , impregnated with 5% Carbowax 1500; carrier gas argon).

RESULTS AND DISCUSSION

In the present work, for the first time we investigated the activity of a complex of Cr(IV) with pyridinium $\text{C}_5\text{H}_5\text{NHCrO}_3\text{Cl}$ [14, 15] as a photocatalyst for the oxidation of saturated hydrocarbons by atmospheric oxygen. Cyclohexane was selected as the substrate, and the solvent was methylene chloride. Unfortunately, the complete insolubility of the complex in acetonitrile did not make it possible to use this solvent or to make a comparison with certain processes catalysed by Cr(VI) oxocomplexes [9]. It must be noted that the solubility of the Cr(IV) complex investigated in methylene chloride is also very low, and the solution used for the photo-oxidation of cyclohexane is saturated in relation to the catalyst.

We found that, in the case of the filament-lamp light irradiation in air of a solution of cyclohexane in CH_2Cl_2 in the presence of a Cr(IV) complex, the oxidation of the hydrocarbon occurs with the formation of cyclohexanol and cyclohexanone. The accumulation of products in time is shown in Fig. 1. As can be seen, the formation of alcohol and ketone occurs in parallel and ends after 3 hr. In this time, roughly eight molecules of the products are produced per photocatalyst molecule. In the absorption spectrum of the reaction solution over the course of oxidation there is a gradual reduction in absorption in the $\lambda > 370$ nm region and an increase in absorption in the shorter wave region from this isobestic point. These changes occurring in the first 3–4 hr of the reaction evidently reflect conversions of the complex that ultimately lead to loss of its catalytic activity. It can be assumed that activity is lost as a result of reduction of the complex to the Cr(III) derivative.

It is extremely significant that in this reaction, neither in the developed period nor at the very start, is an appreciable concentration of cyclohexylhydroperoxide formed (analysed after reduction to cyclohexanol by triphenylphosphine, as described in [1]). Similarly, the absence of cyclohexylhydroperoxide was observed in oxygenation photocatalysed by polyoxochro-

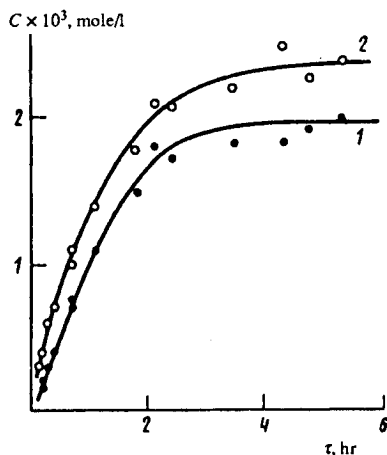


FIG. 1. Accumulation of cyclohexanol (1) and cyclohexanone (2) in time during the photo-oxidation of cyclohexane (0.37 mole/l) in CH_2Cl_2 in the presence of complex $\text{C}_5\text{H}_5\text{NHCrO}_2\text{Cl}$ (5×10^{-4} mole/l). Data from three independent experiments were used to plot the curves.

mates [13]. Evidently, in contrast to chloride derivatives of iron and gold and polytungstate [1], chromium compounds exhibit high activity in the decomposition of alkylhydroperoxide to alcohol and ketone. Such catalysed decomposition can occur both in darkness and under exposure to light.

In this way, the Cr(IV) oxocomplex exhibits activity in the photo-oxygenation of alkanes by oxygen that is comparable with the activity of Cr(VI) oxocomplexes [9, 13],

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