

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION METALS.

22.* POLYCHROMATE-CATALYZED PHOTOOXYGENATION OF ALKANES
AND OTHER COMPOUNDS BY O₂ OF AIR IN CH₂Cl₂

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Irradiation by light with $\lambda > 520$ nm of solutions of cyclohexane, n-hexane, and ethylbenzene in CH₂Cl₂ in air in the presence of the complexes (Bu₄N)₂Cr₂O₇, (Bu₄N)₂Cr₃O₁₀, or (Bu₄N)₂Cr₄O₁₃ results in formation (after GLC) of the corresponding alcohols and ketones. Under these conditions, styrene epoxide, benzaldehyde, and acetophenone are produced from styrene; alcohols are oxidized to carbonyl compounds; and triphenylphosphine forms triphenylphosphine oxide.

One of the fundamentally new methods of selectively and efficiently converting saturated, alkylaromatic, and olefinic hydrocarbons to the desired products [4-7] is low-temperature irradiation (solar radiation) of liquids in the presence of metal-complex catalysts.

Irradiation by light of hydrocarbons in organic acids and aprotic solvents in the presence of Cr(VI) (CrO₃, Cr₂O₇²⁻, etc.) [8-11] and V(V) oxocompounds [12] results in oxygenation of the hydrocarbons. If the hydrocarbon and Cr(VI) oxocompound are irradiated in air in an aprotic solvent at a relatively low concentration of oxocompound, the latter acts not as an oxidant but as a catalyst for photooxygenation by O₂ in air [13-15]. We found that other oxocompounds also have this property: PW₁₂O₄₀³⁻, PV₅Mo₆O₂₇¹²⁻, VO₃⁻, and UO₂²⁺ [13, 16-18]. Thus, oxometallates under irradiation catalyze oxygenation of alkylaromatic compounds even in alcohols [13, 17]. It was discovered almost simultaneously that alkanes and arylalkanes are photooxygenated in the presence of catalytic amounts of iso- and polyoxometallates such as W₁₀O₃₂⁴⁻ and PW₁₂O₄₀³⁻ [19-21]. It is notable that alkanes are converted into alkenes in the complete absence of O₂ by photoexcited oxometallate particles [22].

EXPERIMENTAL

The complexes and photocatalysts (Bu₄N)₂Cr₂O₇, (Bu₄N)₂Cr₃O₁₀, and (Bu₄N)₂Cr₄O₁₃ were prepared as before [23, 24]. The reactions were carried out in glass cylinders at -5°C with constant stirring by a magnetic stirrer and irradiation by light from a mercury lamp (250 W) that was filtered through an aqueous solution of K₂Cr₂O₇ ($\lambda > 520$ nm). The product yield was measured by GLC (LKhM-80-6 chromatograph, 2 m × 4 mm column filled with Inerton AW-HMDS, 0.25-0.315 mm coated with 5% Carbowax 1500) or TLC on Silufol UV-254 (the product band was scraped off, washed with CHCl₃, and analyzed for product concentration spectrophotometrically on a Specord UV-VIS instrument).

RESULTS AND DISCUSSION

Irradiation by light with $\lambda > 520$ nm of a solution of cyclohexane in CH₂Cl₂ at 5°C in air in the presence of tetrabutylammonium oxochromate produces cyclohexanol and cyclohexanone in approximately equal amounts (Fig. 1).† The oxygenation products accumulate after an induction period that is especially long for Cr₂O₇²⁻ and almost undetectable for Cr₄O₁₃²⁻. If the solution of (Bu₄N)₂Cr₂O₇ in CH₂Cl₂ is irradiated for 100 min before addition of cyclohexane, the hydrocarbon is oxidized without an induction period (Fig. 1c).

*For previous communication, see [1]. Preliminary reports have been published [2, 3].

†The cyclohexylhydroperoxide formed in this reaction decomposes during chromatography to give cyclohexanol and cyclohexanone.

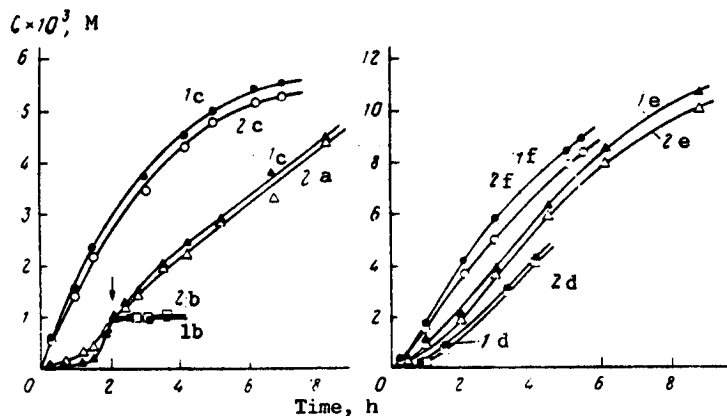


Fig. 1. Kinetic curves of cyclohexanol (1) and cyclohexanone (2) production during photooxygenation of a solution of cyclohexane (0.46 M) in CH_2Cl_2 in the presence of: $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$ ($2.5 \cdot 10^{-4}$ M) (a), the same but with irradiation stopped at the time indicated by the arrow (b), the same catalyst irradiated for 100 min before addition of cyclohexane (c), $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$ ($5 \cdot 10^{-4}$ M) (d), $(\text{Bu}_4\text{N})_2\text{Cr}_3\text{O}_{10}$ ($5 \cdot 10^{-4}$ M) (e), $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ ($5 \cdot 10^{-4}$ M) (f).

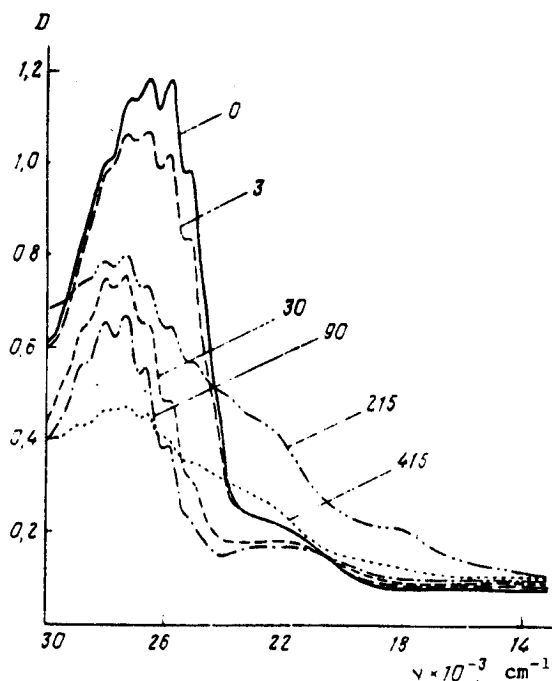


Fig. 2. Absorption spectra of a reaction mixture during photooxygenation of cyclohexane in the presence of $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$ ($5 \cdot 10^{-4}$ M). Numbers of the spectra indicate irradiation time in min.

Changes in the absorption spectra of the solution during the photooxygenation of cyclohexane in the presence of $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$ are plotted in Fig. 2. The absorption near $\sim 27,000 \text{ cm}^{-1}$ drops sharply even in the first minutes of the induction period when product formation is not observed. The band maximum simultaneously shifts to shorter wavelength. After about 90 min the absorption spectrum corresponds to that of $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$. It is noteworthy that the decrease of absorption in the middle of the band is accompanied by an increase in the long-wavelength region (Fig. 3). An isosbestic point is found at $20,880 \text{ cm}^{-1}$. After ~ 100 min oxygenation products begin to accumulate almost linearly. However, the spectra of the solution change significantly during this period. Absorption near $22,800$ and $18,400 \text{ cm}^{-1}$ initially increases and then decreases. New bands appear in these ranges. It should be noted that the spectra indicate that $\text{Cr}_2\text{O}_7^{2-}$ converts into $\text{Cr}_4\text{O}_{13}^{2-}$ during irradiation even

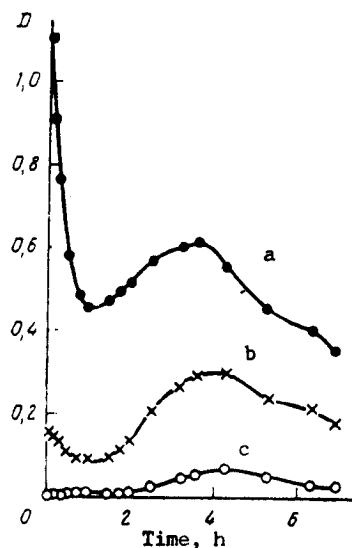


Fig. 3

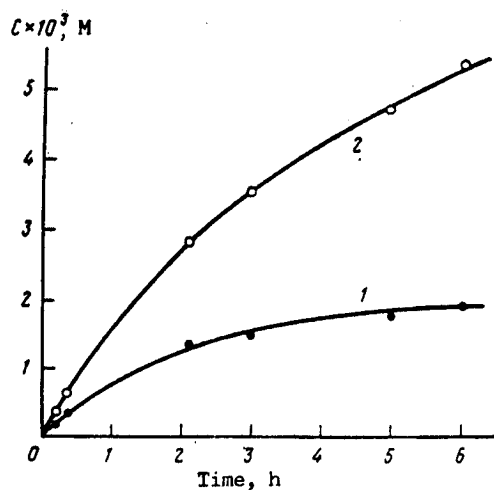


Fig. 4

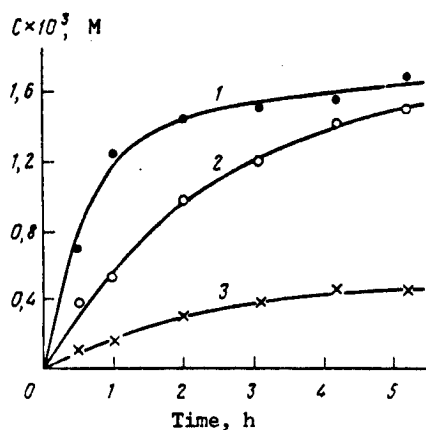


Fig. 5

Fig. 3. Dependence of absorption D on reaction time at $\lambda = 26,640$ (a), $22,800$ (b), and $18,400$ cm^{-1} (c) during photooxygenation of cyclohexane in the presence of $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$ ($5 \cdot 10^{-4}$ M).

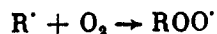
Fig. 4. Kinetic curves of 1-phenylethanol (1) and acetophenone (2) production during photooxygenation of a solution of ethylbenzene (0.46 M) in CH_2Cl_2 in the presence of $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ ($5 \cdot 10^{-4}$ M).

Fig. 5. Kinetic curves of styrene epoxide (1), benzaldehyde (2), and acetophenone (3) production during photooxygenation of a solution of styrene (0.1 M) in CH_2Cl_2 in the presence of $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ ($5 \cdot 10^{-4}$ M).

in the absence of cyclohexane. Therefore, it can be concluded that the dinuclear $\text{Cr}_2\text{O}_7^{2-}$ ion does not catalyze the photooxygenation of cyclohexane. However, $(\text{Bu}_4\text{N})_2\text{Cr}_2\text{O}_7$ does polymerize during irradiation to form, for example, the tetranuclear $(\text{Bu}_4\text{N})_2\text{Cr}_4\text{O}_{13}$ complex, which can oxygenate the alkane. Apparently the polynuclear photoexcited complex, in contrast with the dinuclear one, can abstract a H from the alkane according to



The electron acquired by the complex is distributed over the polynuclear framework. As a result, a so-called blue reduced form of the polyoxometallate forms [25]. The absorption bands at $22,800$ and $18,400$ cm^{-1} can be assigned to this reduced form. The alkyl radical rapidly reacts with O_2 , converting to the peroxide radical:



The reduced polyoxochromate can be reoxidized by this radical. As a result, the starting catalytically active polychromate complex and hydroperoxide are generated. The latter can be converted by the complex and light into the final products, alcohol and ketone. It should be noted that the complex decomposes during the reaction, losing its catalytic activity after about 20 h of irradiation. The proposed mechanism of oxygenation is confirmed by the following experiment. Irradiation of a solution of cyclohexane and $(Bu_4N)_2Cr_4O_{13}$ ($5 \cdot 10^{-4}$ M) in CH_2Cl_2 under Ar (solvent and substrate were previously distilled under Ar) did not produce noticeable amounts of cyclohexanol and cyclohexanone. However, after a long induction period (greater than 3 h) cyclohexyl chloride is detected ($\sim 5 \cdot 10^{-4}$ M). This product can be formed by reaction of alkyl radicals with CH_2Cl_2 .

A study of the oxygenation of cyclohexane in the presence of $Cr_4O_{13}^{2-}$ at various temperatures between 3-30°C demonstrated that the rate of the process depends very weakly on temperature. The effective activation energy $E_a < 20$ kJ/mole. The initial rate of product formation was much greater during irradiation of solutions of polychromates and cyclohexane by light with $\lambda > 450$ nm (no induction period) than during irradiation using the $K_2Cr_2O_7$ filter. However, a green insoluble precipitate begins to separate and the oxygenation stops after only ~ 0.5 h.

It is interesting that the monochromate practically does not catalyze the photooxygenation of cyclohexane. Thus, only $8 \cdot 10^{-4}$ M cyclohexanol and $6 \cdot 10^{-4}$ M cyclohexanone are formed after 5 h in the presence of $5 \cdot 10^{-4}$ M $(Bu_4N)_2CrO_4$. If CH_3CN is used as solvent, $(Bu_4N)_2Cr_2O_7$ does not catalyze photooxygenation of cyclohexane.

Oxygenation of n-hexane (0.46 M) during irradiation in CH_2Cl_2 in the presence of $5 \cdot 10^{-4}$ M $(Bu_4N)_2Cr_4O_{13}$ gives after 7 h up to $1.5 \cdot 10^{-4}$ M 1-hexanol, $1 \cdot 10^{-3}$ M of a mixture of 2-hexanol and 3-hexanol, $2.3 \cdot 10^{-4}$ M hexanal, and $2.8 \cdot 10^{-3}$ M of a mixture of 2-hexanone and 3-hexanone. The kinetics of 1-phenylethanol and acetophenone production during oxidation of ethylbenzene are plotted in Fig. 4. Besides these products, a small amount of 1-chloroethylbenzene was found in the mixture. Photooxidation of styrene produces the epoxide, benzaldehyde, and acetophenone (Fig. 5). Benzyl alcohol (0.46 M) after 3-h irradiation in the presence of $2.5 \cdot 10^{-4}$ M $(Bu_4N)_2Cr_2O_7$ forms $8 \cdot 10^{-3}$ M benzaldehyde. Finally, triphenylphosphine ($4.3 \cdot 10^{-3}$ M) quantitatively converts to triphenylphosphine oxide during irradiation under these same conditions.

In conclusion, it is noteworthy that an attempt to photooxygenate cyclohexane by the peroxide complex of Cr(VI) $(C_5H_5N)CrO_5$ ($5 \cdot 10^{-4}$ M) in CH_2Cl_2 during irradiation by light with $\lambda > 450$ nm converts the peroxide complex in the first 15 min to a poorly soluble orange pyridine derivative of Cr(VI). Only after this does oxygenation of cyclohexane by O_2 in air begin. This is catalyzed by the solid Cr(VI) oxocompound. After 6 h, $2.8 \cdot 10^{-3}$ M cyclohexanol and $3 \cdot 10^{-3}$ M cyclohexanone are formed.

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