

CONTRIBUTION OF AIR OXYGEN TO PHOTOOXIDATION OF ALKANES  
BY VANADIUM(V) AND CHROMIUM(VI) OXOCOMPLEXES

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In photochemical oxygenation of cyclohexane by  $KVO_3$ - $CF_3COOH$  or  $K_2Cr_2O_7$ - $Bu_4NBr$ - $H_2O$ - $CH_2Cl_2$  in air the source of oxygen atoms in the product cyclohexanol and cyclohexanone is air dioxygen rather than a metal oxo-complex. In the absence of dioxygen the products of alkane oxygenation are not formed in either of the above systems. At  $pH = 3$ ,  $Cr(VI)$  does oxidize cyclohexane to cyclohexanol even in argon atmosphere.

В реакции фотохимического окисления циклогексана в системах  $KVO_3$ - $CF_3COOH$  или  $K_2Cr_2O_7$ - $Bu_4NBr$ - $H_2O$ - $CH_2Cl_2$  на воздухе источником кислородного атома в образующихся циклогексаноле и циклогексаноне является диоксиген воздуха, а не оксокомплекс металла. В отсутствие диоксигена продукты окисления алкана не образуются в обеих системах. Однако, при  $pH=3$ ,  $Cr(VI)$  окисляет циклогексан до циклогексанола даже в атмосфере аргона.

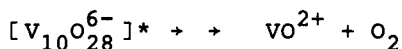
Oxocompounds of high-valent metals are suitable reactants for oxygenation of alkanes and arylalkanes [1,2]. Recently we have reported that alkanes can easily be oxidized when solutions of alkanes and oxocomplexes, in particular  $VO_3^-$  in  $CF_3COOH$  [3],  $(Bu_4N)_2Cr_4O_{13}$  in  $CH_2Cl_2$  [4], and  $K_2Cr_2O_7$ - $Bu_4NBr$  in  $CH_2Cl_2$ - $H_2O$  [5], are irradiated in air.

The results of our present study indicate that the reaction between polyoxovanadate formed when  $KVO_3$  is dissolved in  $CF_3COOH$  [6-8], and cyclohexane under irradiation yields two products: cyclohexanone and cyclohexyl trifluoroacetate. The latter was detected after hydrolysis as cyclohexanol. Reactions were carried out in a Pyrex cylindrical vessel with a water-cooled ( $\sim 10^\circ C$ ) jacket under stirring. The total volume of the reaction solution was  $10\text{ cm}^3$ . The source of irradiation was a luminescent street lamp (250 W). Products were identified by gas-liquid chromatography.

The formation rate of oxidation products is higher when the reaction is carried out in dioxygen atmosphere (Fig. 1). It should be noted that in the absence of dioxygen no cyclohexane oxidation products are formed.

The orange reaction solution at the end of irradiation becomes light green due to the formation of V(IV) compounds. Changes in the absorption spectrum of the reaction solution during photooxidation in air are illustrated in Fig. 2. The growth of absorption at 700 and 580 nm is apparently due to the accumulation of reduced polyvanadate and isopolyblue (see e.g. [6,9,10]). A similar absorption band at 700 nm and a shoulder at 580 nm arise in the spectrum if ethylbenzene is added to the solution of  $KVO_3$  in  $CF_3COOH$  without irradiation. After 1 h irradiation of the cyclohexane solution, the absorption at  $\lambda > 500$  nm decreases and finally at reaction times above 3 h the spectrum of a V(IV) compound is observed. It should be noted that in the absence of cyclohexane in air or argon atmosphere, polyvanadate in  $CF_3COOH$  under irradiation is reduced to a V(IV) compound, which can be observed in the absorption spectra. This process is apparently accompanied by dioxygen evolution.

The following reaction mechanism can be suggested. Under irradiation, polyvanadate  $V_{10}O_{28}^{6-}$  transforms to an excited species that in the absence of alkane is reduced to yield finally V(IV) and  $O_2$



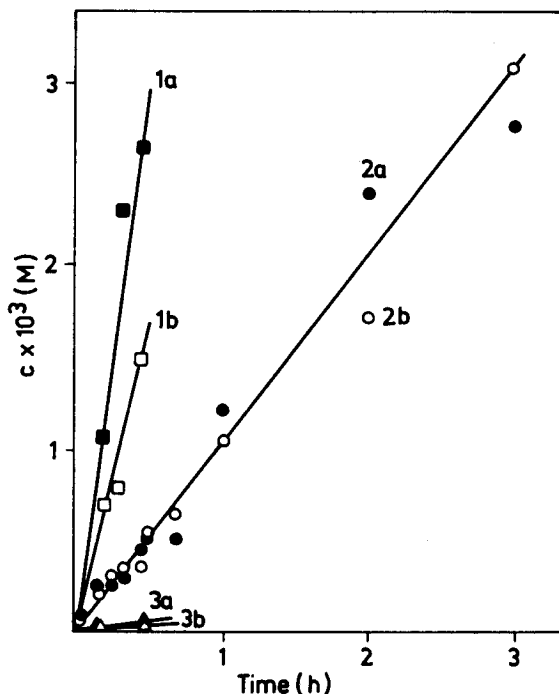
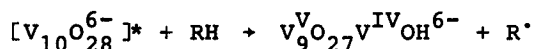


Fig. 1. Kinetics of cyclohexane (0.46 M) oxygenation by  $KVO_3$  (0.2 M) in  $CF_3COOH$  under irradiation in dioxygen (1), air (2) and argon (3)  
a - Cyclohexanol, b - cyclohexanone

In the presence of cyclohexane RH the excited species can abstract a hydrogen atom to produce a radical  $R^{\cdot}$  and a reduced form of polyvanadate



Photoreduction of polyoxometalates has been described previously [11-16]. In air radicals  $R^{\cdot}$  react rapidly with  $O_2$



and the reduced polyvanadate gradually transforms to V(V) and V(IV) derivatives. Apparently, the reduced form of polyvanadate

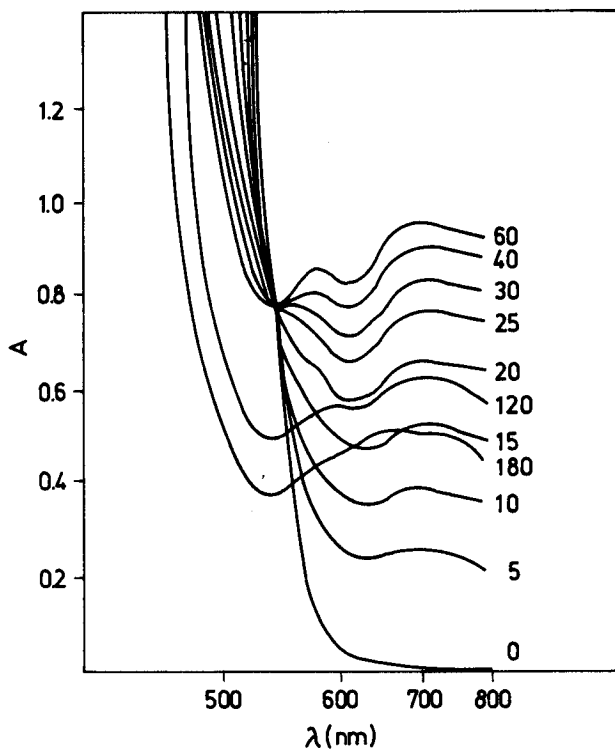
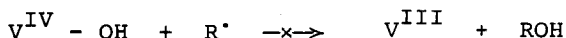


Fig. 2. Changes in spectra (Specord UV-VIS Spectrometer) of reaction solutions of  $KVO_3$  and cyclohexane in  $CF_3COOH$  under irradiation in air (see curve 2, Fig. 1). Numerals correspond to the minutes from the beginning of irradiation

can be reoxidized by dioxygen or peroxide radicals. Indeed, when polyvanadate is used in small concentrations ( $4 \times 10^{-4}$  M) in  $CF_3COOH$ , after 3 h irradiation in air the yield of cyclohexanol and cyclohexanone per V(V) is much higher than 100%, namely 1.1 and 6 mol per 1 mol V(V), respectively.  $VO_3^-$  ion is known to be a catalyst for photooxygenation in aprotic organic solvents [16].

In the absence of dioxygen neither cyclohexanol nor cyclohexanone are, however, formed. Hence the reaction between alkyl

radicals and reduced polyoxovanadate



is impossible. In this case radicals  $R^{\cdot}$  can produce olefins  $R(-H)$  or  $RR$ .

Thus during the photooxygenation of cyclohexane by a  $V^V=O$  complex in air that yields cyclohexanol, cyclohexanone and a  $V^{IV}=O$  derivative, an oxygen atom from dioxygen (rather than from  $V^V=O$ ) inserts into the C-H bond of alkane.

We have also investigated the photooxidation of cyclohexane by  $K_2Cr_2O_7$  in a biphasic system  $H_2O-CH_2Cl_2$  in the presence of  $Bu_4NBr$  (in the same reaction conditions as for polyvanadate). This reaction carried out in air yields cyclohexanol, cyclohexanone and small amounts of cyclohexyl chloride (Fig. 3). After 3 h irradiation all  $Cr(VI)$  transforms to  $Cr(III)$ , which is confirmed by changes in the absorption spectrum of the reaction solution.

When the reaction is carried out in argon atmosphere, after 3 h irradiation, only very small amounts of cyclohexanol ( $0.5 \times 10^{-6}$  mol), cyclohexanone ( $0.6 \times 10^{-6}$  mol) and cyclohexyl chloride ( $3.2 \times 10^{-6}$  mol) are formed. It is interesting that in this case the transformation  $Cr(VI) \rightarrow Cr(III)$  was not observed in the absorption spectrum after 3 h. But if  $H_2SO_4$  is added to an aqueous solution of  $K_2Cr_2O_7$  ( $pH = 3$ ), even in argon atmosphere all  $Cr(VI)$  transforms to  $Cr(III)$  after 2 h irradiation, producing a significant amount of cyclohexanol ( $1.2 \times 10^{-5}$  mol), considerably lower amounts of cyclohexanone ( $1.1 \times 10^{-6}$  mol) and cyclohexyl chloride ( $4.6 \times 10^{-6}$  mol).

The results can be interpreted as follows. In air the photoexcited  $Cr(VI)$  species abstracts a hydrogen atom from the alkane  $RH$



and then  $R^{\cdot}$  reacts with  $O_2$  to yield alcohol and ketone as is described above, and  $Cr(V)$  produces  $Cr(VI)$  and  $Cr(III)$ . Hence the overall reaction can be written as

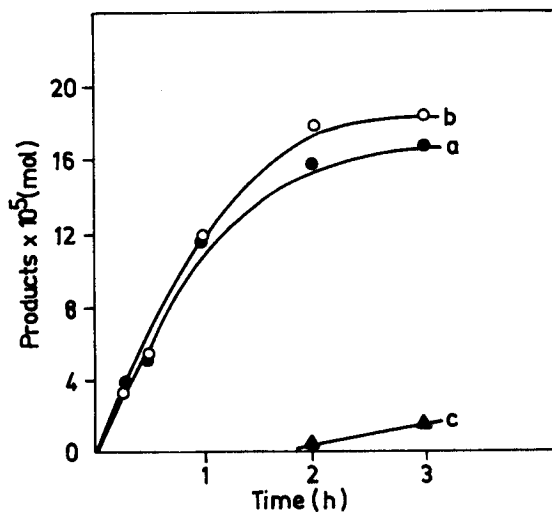
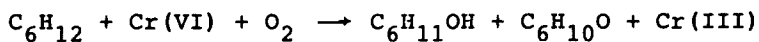


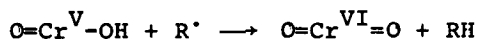
Fig. 3. Kinetics of cyclohexane ( $0.5 \text{ cm}^3$ ) oxygenation by  $\text{K}_2\text{Cr}_2\text{O}_7$  ( $2.5 \times 10^{-5} \text{ mol}$ ) in  $\text{CH}_2\text{Cl}_2$  ( $4.5 \text{ cm}^3$ ) -  $\text{H}_2\text{O}$  ( $5 \text{ cm}^3$ ) in the presence of  $2 \times 10^{-5} \text{ mol}$   $\text{Bu}_4\text{NBr}$  in air under irradiation  
 a - Cyclohexanol, b - cyclohexanone, c - cyclohexyl chloride



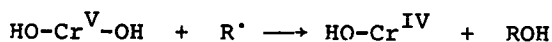
Radicals  $\text{R}^\cdot$  can also react with  $\text{CH}_2\text{Cl}_2$



In the absence of dioxygen the interaction between  $\text{Cr(VI)}$  and  $\text{RH}$  can be reversible and the radicals  $\text{R}^\cdot$  react with  $\text{CH}_2\text{Cl}_2$  and mainly with  $\text{Cr(V)}$

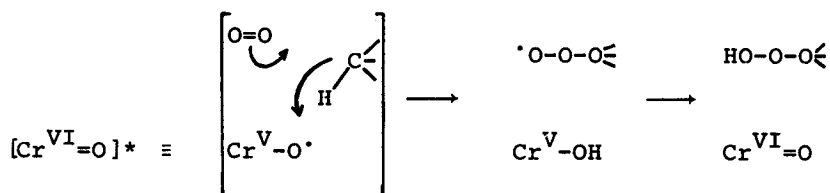


The reaction route changes in acidic media. One can assume that the radical  $\text{R}^\cdot$  is able to detach  $\text{OH}$  from the protonated  $\text{Cr(V)}$  species



This step was proposed for the mechanism of thermal oxidation of alkanes by Cr(VI) in acidic media [1,17].

An alternative interpretation for the contribution of dioxygen implies that the reaction proceeds mainly via a transition state involving a dioxygen molecule



It is evident that in this case the Cr(VI) oxocomplex can catalyze the photooxygenation of alkanes by dioxygen [5].

It should be noted that in the manganese porphyrin catalyzed oxygenation of alkanes by iodosylbenzene the ketone/alcohol ratio changes when air is substituted by argon [18]. The participation of air dioxygen was established for the thermal oxygenation of ethylbenzene by iodosylbenzene catalyzed by  $\text{CrO}_3$  [19]. In all these cases the suggested mechanism includes the abstraction of a hydrogen atom from RH by a high-valent metal oxocomplex and the subsequent reaction of  $\text{R}^{\cdot}$  with  $\text{O}_2$  [20]. A similar mechanism can be assumed for some routes of the biological oxygenation catalyzed by P-450 [1,21].

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