

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS

WITH TRANSITION-METAL COMPLEXES.

XIII.\* OXIDATION OF ALKYL BENZENES WITH OXYGEN CATALYZED  
BY POLYOXOMETALATE IONS

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Continuing our systematic study of the photochemical activation of the C-H bond by oxo compounds of transition metals [1-3], we have investigated the reactions of polyoxometalate ions with alkylaromatic hydrocarbons under irradiation. Heteropoly acids are widely used in catalysis [4-8]. The photoactivity of iso- and heteropoly compounds is well known, particularly in the oxidation of various organic substrates [9-23]. Thus, the photochemical reactions of the alkanes RH with acetonitrile under irradiation in presence of polyoxometalate ions lead to the formation of RNHCOCH<sub>3</sub>, RCOCH<sub>3</sub>, alkenes, and H<sub>2</sub> [24].

We have found that in the irradiation of a solution of a polyoxometalate in acetic acid with toluene or ethylbenzene benzaldehyde or acetophenone is formed. Unless specially stipulated we used  $0.83 \cdot 10^{-5}$  mole of the polyoxometalate in 5 ml of reaction space containing 0.5 ml of the hydrocarbon, and the irradiation time was 2 h. The irradiation was conducted in a glass vessel with the total radiation of a high-pressure mercury lamp ( $\lambda > 300$  nm). The yield of oxidation product was then about 6 moles per mole of the polyoxometalate (Table 1). When the reaction was conducted in an atmosphere of argon in previously deaerated solvents, the yield of benzaldehyde fell to about 1 mole per mole of the polyoxometalate (we investigated  $\text{PMo}_{11}\text{VO}_{40}^{4-}$  and  $\text{PW}_{12}\text{O}_{40}^{3-}$ ). Hence, the alkylbenzenes are oxidized by atmospheric oxygen dissolved in acetic acid, while the polyoxometalate plays the part of a catalyst. In "deaerated" acetic acid oxidation probably proceeds on account of the very small amount of oxygen that finds its way into the solution during the mixing of the components and the performance of the reaction itself. It should be noted that in the case of most polyoxometalate ions on irradiation with toluene even in air the formation of blue solutions of reduced forms of hetero- and isopolyoxometalates is observed. Only in the case of  $\text{PW}_{12}\text{O}_{40}^{3-}$  does the solution remain practically colorless throughout the reaction in air. If, however, the reaction with this ion is conducted in an atmosphere of argon, the solution assumes a blue color after only a few minutes from the start of the irradiation, but the color rapidly disappears when a little air enters the vessel. It should be noted also that, in the oxidation of toluene, as well as benzaldehyde, benzyl alcohol is formed; its amount does not exceed 20% of the amount of benzaldehyde.

As follows from Table 1, the rate of oxidation of the alkylbenzenes is little dependent on the nature of the heteropolyoxometalate and scarcely changes on the introduction of vanadium atoms into the molecule. When the isopolyoxometalate  $\text{Mo}_7\text{O}_{24}^{6-}$  is used, the reaction

\*For communication XII, see [1].

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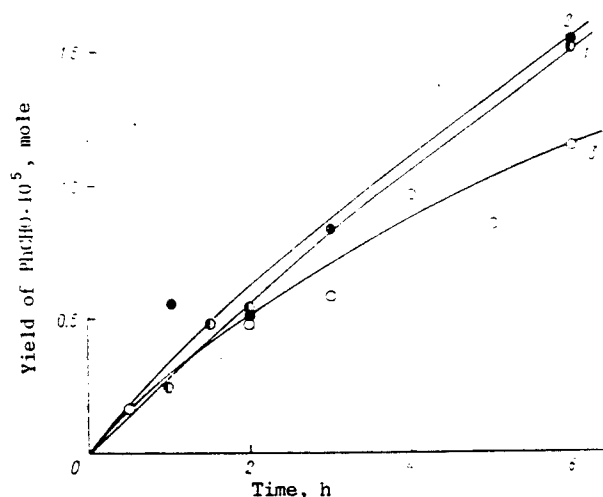


Fig. 1. Accumulation of benzaldehyde in the photochemical oxidation of a solution of toluene (0.5 ml) in  $\text{CH}_3\text{COOH}$  (total volume of solution 5 ml) with oxygen in presence of polyoxometalate ions ( $0.83 \cdot 10^{-5}$  mole): 1)  $\text{PW}_{12}\text{O}_{40}^{3-}$ ; 2)  $\text{PMo}_{11}\text{VO}_{40}^{4-}$ ; 3)  $\text{PMo}_5\text{V}_5\text{O}_{39}^{12-}$ .

TABLE 1. Products of the Oxidation ( $\cdot 10^5$  mole) of Toluene and Ethylbenzene in  $\text{CH}_3\text{COOH}$  after Irradiation for 2 h

Polyoxometalate, $0.83 \cdot 10^{-6}$ mole	Benzaldehyde	Acetophenone	Polyoxometalate, $0.83 \cdot 10^{-6}$ mole	Benzaldehyde	Acetophenone
$\text{PMo}_{12}\text{O}_{40}^{3-}$	5.0	5.0	$\text{PW}_{12}\text{O}_{40}^{3-}$	5.3	8.4
$\text{PMo}_{11}\text{VO}_{40}^{4-}$	5.0	8.3	$\text{SiW}_{12}\text{O}_{40}^{4-}$	4.0	5.8
$\text{PMo}_5\text{V}_5\text{O}_{39}^{12-}$	4.9	7.7	$\text{Mo}_7\text{O}_{24}^{2-}$	2.5	

rate is halved. The accumulation of benzaldehyde in the oxidation of toluene in presence of  $\text{PW}_{12}\text{O}_{40}^{3-}$ ,  $\text{PMo}_{11}\text{VO}_{40}^{4-}$ , and  $\text{PMo}_5\text{V}_5\text{O}_{39}^{12-}$  ions proceeds by a linear law (see Fig. 1). The maximum yield of benzaldehyde after irradiation for 6 h attains 18 moles per mole of the polyoxometalate.

Taking the oxidation reaction of toluene in presence of the  $\text{PW}_{12}\text{O}_{40}^{3-}$  ion as our example, we showed that the reaction is of first order with respect to the hydrocarbon.

Amount of toluene ( $\cdot 10^3$ mole)	0	0.95	1.88	2.82	4.70
Amount of benzaldehyde ( $\cdot 10^6$ mole)	0	2.2	2.6	3.8	5.3

Investigation of the relation of the yield of benzaldehyde after irradiation for 2 h at a constant initial amount of toluene ( $4.7 \cdot 10^{-3}$  mole) to the initial amounts of the  $\text{PMo}_{11}\text{VO}_{40}^{4-}$  ion showed that, whereas at low concentrations of the polyoxometalate with increase in its amount the absolute yield (in moles) of benzaldehyde increases, after this the amount of benzaldehyde formed practically ceases to depend on the initial concentration of  $\text{PMo}_{11}\text{VO}_{40}^{4-}$ .

Amount of $\text{PMo}_{11}\text{VO}_{40}^{4-}$ ( $\cdot 10^5$ mole)	0	0.22	0.42	0.83	2.5	11.6
Amount of benzaldehyde ( $\cdot 10^6$ mole)	0	3.0	5.5	5.0	8.3	9.1

With the use of metal gauzes that absorb a definite fraction of the light falling on the reaction mixture, it was established that in the oxidation of toluene in presence of the  $\text{PW}_{12}\text{O}_{40}^{3-}$  ion the yield of benzaldehyde depends linearly on the intensity of the light (the intensity of the light I without the use of the gauzes was taken to be 100%).

Intensity of light I, %	100	45	30	0
Amount of benzaldehyde ( $\cdot 10^6$ mole)	5.3	3.2	1.5	0

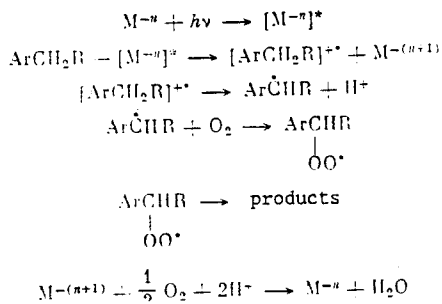
On irradiation with the use of an FS-1 light filter, which passes light with  $\lambda$  from 322 to 485 nm the yield of benzaldehyde in the case of  $PW_{12}O_{40}^{3-}$  falls to  $1.6 \cdot 10^{-5}$  mole. On the other hand, the decrease in the yield of PhCHO in the case of  $PMo_{11}VO_{40}^{3-}$  (to  $4.1 \cdot 10^{-5}$  mole) is only slight. The difference in the behaviors of the two heteropoly compounds is probably to be explained by the fact that, unlike the  $PW_{12}O_{40}^{3-}$  ion, the ion containing the vanadium atom has a red color, and light of lower energy is sufficient for its excitation.

We also investigated the photooxidation of toluene in presence of the  $PW_{12}O_{40}^{3-}$  ion ( $0.83 \cdot 10^{-5}$  mole) with the use of other solvents. Below we give the yields of PhCHO ( $\cdot 10^4$  mole) after irradiation for 2 h in various solvents.

$CH_3COOH$	5.3	$CH_3COCH_3$	3.2
$(CH_3)_2CHOH$	4.2	$C_6H_5OH$	2.5
$CH_3OH$	3.2	$(CH_3)_2SO$	1.4

It can be seen that the highest yields are attained in acetic acid, but in the change from isopropyl alcohol to methanol the amount of benzaldehyde formed decreases only slightly. It should be noted that in alcohols acetals are formed as well as benzaldehyde, but in analysis these are converted by alkaline hydrolysis into benzaldehyde. Also, in this case, chromatography on Silufol plates shows that the reaction mixture contains a number of unidentified products.

The mechanism proposed for the reaction described includes the excitation of the polyoxometalate ion  $M^{n-}$  by light, after which there occurs the transfer of an electron from the alkylaromatic compounds to the excited species  $[M^{n-}]^*$ . The radical cation loses a proton, and the arylalkyl radical formed reacts with dissolved oxygen with the formation of hydroperoxides, which then decompose with the formation of products of the oxidation of the alkylbenzene: aldehydes or ketones. The reduced form of the polyoxometalate ion is oxidized by oxygen to the original state, and then the cycle is repeated.



An analogous mechanism was proposed for the process of the photooxidation of alkylbenzenes in presence of 9,10-anthracenedicarbonitrile [25] or 1,4-naphthalenedicarbonitrile [26]. It was shown in [25] that in such reactions singlet oxygen or the superoxide ion does not participate.

#### EXPERIMENTAL

The irradiation of the samples was effected with the light from a DRSh-1000 high-pressure mercury lamp (1000 W) in a glass cylindrical vessel provided with a jacket for cooling with running water ( $12 \pm 2^\circ C$ ). The reaction mixture was agitated constantly with a magnetic stirrer. The determination of the amount of benzaldehyde or acetophenone formed was conducted as described earlier [1]. We used the commercial reagents  $H_3PMo_{12}O_{40}$ ,  $H_3PW_{12}O_{40}$ ,  $H_4SiW_{12}O_{40}$ ; samples of solutions of  $H_4PMo_{11}VO_{40}$  and  $H_5Na_7PMo_5V_5O_{39}$  were prepared at the Institute of Catalysis, Siberian Branch, Academy of Sciences of the USSR (Novosibirsk).

#### CONCLUSIONS

The photochemical reactions of alkylbenzenes with oxygen in presence of catalytic amounts of heteropoly acids go with the formation of products of the oxidation of the alkyl side group, mainly aldehydes and ketones.

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