

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION-METAL COMPLEXES.

XIV.\* PHOTOOXIDATION OF TOLUENE TO BENZALDEHYDE WITH OXYGEN  
IN CH<sub>3</sub>COOH CATALYZED BY FeCl<sub>3</sub> AND PHENANTHROLINE

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547.53

Among photochemical processes catalyzed (sensitized) by organic [2-4] and metal-complex [5] compounds a special place is occupied by the oxidation reaction of organic substrates by molecular oxygen. The oxidation of olefins has been best studied (see, e.g., [6, 7]). In recent years alkylaromatic [8-10] and saturated [11, 12] hydrocarbons have been used as substrates. The investigation of photocatalytic processes with the breakage of a C-H bond [13] with the participation of molecular oxygen is important for several reasons: 1) There is the prospect of the development of new methods for the chemical treatment of hydrocarbon raw material, including inert alkanes; 2) solar energy can be applied for the performance of such chemical processes; 3) these reactions model oxidation processes of hydrocarbons in natural waters (e.g., seawater) under the action of sunlight (see [11]).

In earlier work [1] we showed that alkylbenzenes are oxidized by oxygen dissolved in CH<sub>3</sub>COOH when their solutions are irradiated in presence of catalytic amounts of polyoxo-metalate ions. In the present work we have extended the range of photocatalysts for the

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\*For communication XIII see [1].

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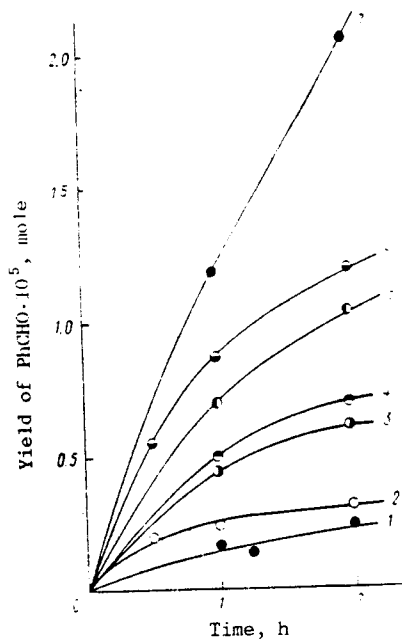


Fig. 1

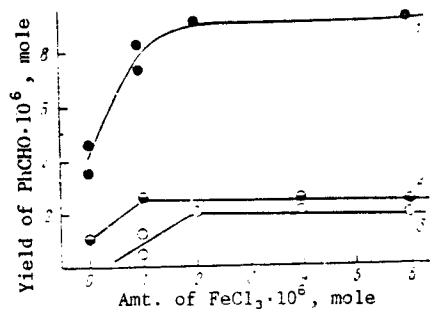


Fig. 2

Fig. 1. Kinetic curves of the oxidation of toluene to benzaldehyde with oxygen dissolved in  $\text{CH}_3\text{COOH}$  with irradiation with the total radiation of a high-pressure mercury lamp in presence of additives (mole): 1)  $\text{VOSO}_4$  ( $1.0 \cdot 10^{-6}$ ); 2)  $\text{FeCl}_3$  ( $1.0 \cdot 10^{-6}$ ); 3) phenanthroline ( $2.0 \cdot 10^{-6}$ ); 4)  $\text{VOSO}_4$  ( $1.0 \cdot 10^{-6}$ ) and phenanthroline ( $2.0 \cdot 10^{-6}$ ); 5) phenanthroline ( $2.0 \cdot 10^{-5}$ ); 6)  $\text{FeCl}_3$  ( $1.0 \cdot 10^{-6}$ ) and phenanthroline ( $2.0 \cdot 10^{-6}$ ); 7)  $\text{VOSO}_4$  ( $1.0 \cdot 10^{-6}$ ) and phenanthroline ( $2.0 \cdot 10^{-5}$ ). The conditions are given in the text.

Fig. 2. Relation of the yield of benzaldehyde to the amount of  $\text{FeCl}_3$  used in the photooxidation of toluene with oxygen (irradiation for 1 h): 1) with an addition of phenanthroline ( $2.0 \cdot 10^{-6}$  mole); 2) without an addition of phenanthroline; 3) data of curve 1 after the subtraction of data of curve 2 and the yield of benzaldehyde ( $4.5 \cdot 10^{-6}$  mole) obtained in irradiation in presence of only phenanthroline ( $2.0 \cdot 10^{-5}$  mole).

oxidation of alkylaromatic compounds. We report here the first results of an investigation of the photocatalytic properties of a large number of ions of transition metals and tertiary aromatic amines, both separately and also when used in combination.

It is known that the photochemical oxidation of alkylbenzenes in an atmosphere of oxygen results mainly in the formation of carbonyl compounds in yields not exceeding 0.15% [14]. In keeping with these data we found that the irradiation of a solution of 0.5 ml of toluene in a mixture of 4.5 ml of  $\text{CH}_3\text{COOH}$  and 1.0 ml of  $\text{H}_2\text{O}$  in a quartz vessel with the total radiation of a medium-pressure mercury lamp ( $\lambda > 220$  nm) for 1 h leads to the formation of  $6.4 \cdot 10^{-6}$  mole of benzaldehyde. The irradiation of such a solution with a high-pressure mercury lamp in a glass vessel ( $\lambda > 300$  nm) gives a considerably smaller amount of benzaldehyde ( $1.0 \cdot 10^{-6}$  mole). We investigated the influence of additions of metal salts on the yield of the benzaldehyde formed; for this we used a number of chlorides, sulfates, and acetate of transition metals. The results are given in Table 1. It can be seen that the addition of a salt in an amount of  $1.0 \cdot 10^{-6}$  mole usually does not lead to an appreciable rise in the yield of benzaldehyde both when hard UV radiation and when soft UV radiation are used. An exception is found in  $\text{FeCl}_3$ . An addition of this salt leads to about a twofold increase in the yield. It should be noted, however, that in irradiation at  $\lambda > 300$  nm the accumulation of benzaldehyde practically stops after about 2 h (Fig. 1, curve 2), while increase in the amount of  $\text{FeCl}_3$  introduced into the reaction does not lead to an increase in the yield

TABLE 1. Yield of PhCHO ( $\cdot 10^6$  mole) in the Oxidation of Toluene with Oxygen in  $\text{CH}_3\text{COOH}$  Solution on Irradiation for 1 h in Presence of Metal Salts<sup>a</sup>

Added metal salt ( $1.0 \cdot 10^{-6}$ mole)	$\lambda > 220 \text{ nm}$	$\lambda > 300 \text{ nm}$	
		without added phenanthroline	with added phenanthroline ( $2.0 \cdot 10^{-6}$ mole)
None	6.4	1.0	4.5
$\text{FeCl}_3$	10.3	2.5	8.2
$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$	9.6	1.4	3.9
$\text{VOSO}_4$	7.9	1.9	5.0
$\text{CrCl}_3$	8.3	1.2	4.0
$\text{NiCl}_2$			2.5
$\text{MnCl}_2$	6.4	1.0	4.5
$\text{NdCl}_3$			4.0
$\text{RuCl}_3$	4.5	1.4	4.5
$\text{RhCl}_3$	6.5	1.5	3.8
$\text{Cu}(\text{OCOCH}_3)_2$	4.1	1.1	
$\text{Co}(\text{OCOCH}_3)_2$	7.6	1.3	2.4

Note. a) For experimental conditions see text.

TABLE 2. Yield of PhCHO ( $\cdot 10^6$  mole) in the Oxidation of Toluene with Oxygen in  $\text{CH}_3\text{COOH}$  Solution on Irradiation for 1 h in Presence of Organic Compounds and  $\text{FeCl}_3$ <sup>a</sup>

Added organic compound	Amt. of organic compound ( $\cdot 10^6$ mole)	Without additive	With addition of $\text{FeCl}_3$ ( $1.0 \cdot 10^{-6}$ mole)
None	—	1.0	2.5
1,10-Phenanthroline	0.5	1.9	
	2.0	4.5	8.7
2,2'-Bipyridine	20.0	6.9	
	0.5	1.9	
	2.0	4.9	4.5
4,4'-Bipyridine	24.0	4.9	
	2.0	1.6	2.9
Picolinic acid	2.0	1.6	
	30.0	1.6	
Pyridine	2.0	1.8	2.7
Methylviologen	2.0	2.2	
Pyrazole	2.0	2.1	
Phenanthrene	2.0	2.0	2.3

Note. a) For experimental conditions see text.

of benzaldehyde (Fig. 2, curve 2). Vanadyl sulfate also accelerates the photooxidation of toluene only to a small extent (Fig. 1, curve 1).

It was considered important to investigate also the effect of additions of chelating amine ligands capable of binding  $\text{Fe}^{3+}$  and  $\text{VO}^{2+}$  ions into complexes. It was found that on the addition of 1,10-phenanthroline or 2,2'-bipyridine to solutions of  $\text{FeCl}_3$  or  $\text{VOSO}_4$  the yield of benzaldehyde obtained on irradiation rises appreciably. It was also found that, in presence of only 1,10-phenanthroline or 2,2'-bipyridine the photooxidation of toluene to benzaldehyde goes at an appreciable rate (Table 2; Fig. 1, curves 3 and 5; Fig. 3, curve 2). With increase in the amount of amine used in the reaction from 0 to  $2.0 \cdot 10^{-6}$  mole a marked increase is observed in the amount of benzaldehyde formed after irradiation for 1 h. Further increase in the amount of the amine from  $2.0 \cdot 10^{-6}$  to  $2.0 \cdot 10^{-5}$  mole does not lead to a considerable rise in the yield of benzaldehyde. The rate of the accumulation of benzaldehyde falls appreciably on irradiation for 2 h (Fig. 1), which is probably associated with the oxidation of the aromatic amine itself (the photosensitized oxidation of pyridine [15] and photochemical transformations of pyridinium salts [16] are known).

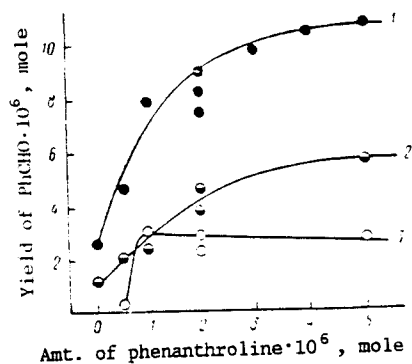


Fig. 3. Relation of the yield of benzaldehyde to the amount of phenanthroline used in the photooxidation of toluene with oxygen (1 h): 1) with an addition of  $\text{FeCl}_3$  ( $1.0 \cdot 10^{-5}$  mole); 2) without an addition of  $\text{FeCl}_3$ ; 3) data of curve 1 after the subtraction of yield of benzaldehyde ( $2.5 \cdot 10^{-6}$  mole) obtained on irradiation in presence of only  $\text{FeCl}_3$  ( $1.0 \cdot 10^{-5}$  mole).

It is characteristic that in presence of other amines (pyridine, picolinic acid, pyrazole) the rate of formation of benzaldehyde is extremely low (Table 2). It is important to emphasize that only aromatic diamines containing nitrogen atoms that are close in space are effective catalysts (sensitizers) of the photooxidation of toluene. In fact, the rate of accumulation of benzaldehyde in presence of 4,4'-bipyridine or its N,N'-dimethyl bis-quaternary compound methylviologen is also low. Also inactive is phenanthrene which, like phenanthroline, has three condensed benzene rings, but differs in not having nitrogen atoms in the rings.

In the case of 2,2'-bipyridine the addition of  $\text{FeCl}_3$  to the amine does not cause increase in the yield of benzaldehyde. A different situation is found when phenanthroline is used. The use simultaneously of phenanthroline and  $\text{FeCl}_3$  as catalyst leads to an appreciable increase in the rate of oxidation, and this rate proves to be considerably greater than the sum of the rates of oxidation in presence of phenanthroline and  $\text{FeCl}_3$  separately. From Figs. 2 and 3 it follows that the maximum effect in the enhancing of the rate of accumulation of benzaldehyde is attained when  $\text{FeCl}_3$  and phenanthroline are introduced into the solution in equal amounts ( $2.0 \cdot 10^{-5}$  or  $1.0 \cdot 10^{-6}$  mole), but there is no further change when a larger amount of  $\text{FeCl}_3$  or phenanthroline is used.

The relation of the yield of benzaldehyde to the amount of phenanthroline and  $\text{FeCl}_3$  introduced into the reaction in 1:1 proportions is linear when the amounts added are small ( $< 3.0 \cdot 10^{-5}$  mole).

Amount of $\text{FeCl}_3$ and phenanthroline (each $\cdot 10^6$ mole)	1	2	2.5	5
Yield of benzaldehyde ( $\cdot 10^6$ mole)	4.3	9.0	8.6	12.2

The relation of the yield of benzaldehyde to the amount of toluene introduced into the reaction is also linear (for amounts of phenanthroline and  $\text{FeCl}_3$  of  $2.0 \cdot 10^{-6}$  and  $1.0 \cdot 10^{-6}$  mole, respectively, 1 h).

Amount of toluene (ml)	0	0.25	0.4	0.5
Yield of benzaldehyde ( $\cdot 10^6$ mole)	0	4.1	5.6	7.3

The rate of oxidation rises with rise in temperature (for the same initial concentrations of phenanthroline and  $\text{FeCl}_3$ , 1 h).

Temperature, $^{\circ}\text{C}$	10	40	70
Yield of benzaldehyde ( $\cdot 10^6$ mole)	7.8	17.6	25.5

An assessment of the effective activation energy of the reaction from these data gave the value  $17 \pm 5$  kJ/mole. Such a value is characteristic for photochemical and radical processes.

The rate of the oxidation reaction is greatly dependent on the acidity of the medium. Thus, the addition of sulfuric acid ( $1.9 \cdot 10^{-5}$  and  $3.7 \cdot 10^{-5}$  mole) to a solution of phenanthroline ( $2.0 \cdot 10^{-5}$  mole) and  $\text{FeCl}_3$  ( $1.0 \cdot 10^{-6}$  mole) increases the yield of benzaldehyde after irradiation for 1 h from  $7.3 \cdot 10^{-6}$  to  $1.4 \cdot 10^{-5}$  and  $3.0 \cdot 10^{-5}$  mole, respectively. On the other hand, the addition of  $1.2 \cdot 10^{-6}$  mole of sodium acetate leads to fall in the yield of benzaldehyde to  $4.9 \cdot 10^{-6}$  mole. The addition of the electron donor p-dimethoxybenzene ( $1.0 \cdot 10^{-5}$  mole) to the solution lowers the yield of benzaldehyde (to  $4.0 \cdot 10^{-6}$  mole after irradiation for 1 h).

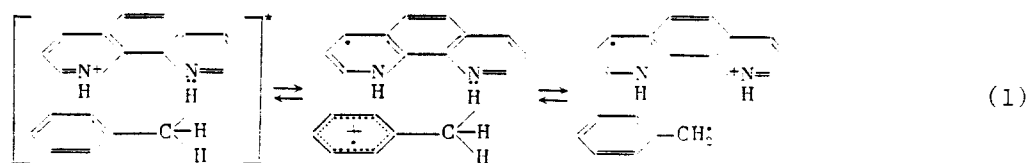
The introduction of electron-donor substituents into the benzene ring of toluene accelerates the oxidation of the methyl group to formyl. By the competing-reactions method we found that the rate of oxidation of p-methoxytoluene is 11 times as high as the rate of oxidation of p-xylene (calculated for 1 methyl group).

As follows from Table 1, the addition of salts of various transition metals to a solution of phenanthroline does not increase the rate of the photooxidation of toluene. A weak accelerating influence was observed only for the  $VO^{2+}$  ion. It is interesting that in presence of  $VO^{2+}$  ions and a considerable amount of phenanthroline ( $2.0 \cdot 10^{-3}$  mole) the rate of the accumulation of benzaldehyde, even after irradiation for 2 h, falls slightly (Fig. 1, curve 7).

Ethylbenzene, when irradiated, is oxidized more rapidly than toluene. In absence of catalysts after irradiation for 1 h from 0.5 ml of ethylbenzene (solution in  $CH_3COOH$ , total volume 6 ml)  $1.3 \cdot 10^{-5}$  mole of acetophenone is formed. On the addition of phenanthroline ( $1.0 \cdot 10^{-6}$  mole) the amount of acetophenone formed rises to  $8.3 \cdot 10^{-5}$  mole. In presence of phenanthroline and  $FeCl_3$  ( $1.0 \cdot 10^{-6}$  mole each) the yield of acetophenone rises to  $1.8 \cdot 10^{-5}$  mole. In presence of only  $FeCl_3$  ( $1.0 \cdot 10^{-6}$  mole)  $6.2 \cdot 10^{-6}$  mole of acetophenone is formed.

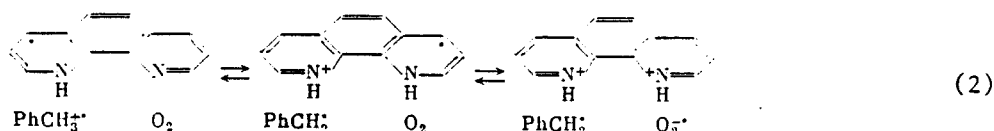
Taking the above-described experimental data and data in the literature on the photooxidation of alkylbenzenes in presence of aryl cyanides [8, 10] into account, we may propose the mechanism given below for the oxidation of toluene in presence of phenanthroline and 2,2'-bipyridine. At the first stage the photoexcitation of the protonated form of the amine occurs. The next stage consists in the transfer of an electron from the toluene molecule to the excited amine species, as a result of which the radical of the amine and the radical cation of toluene are formed. The latter loses a proton, and the benzyl radical formed reacts rapidly with an oxygen molecule with the formation of a peroxide radical. In its turn, this radical can accept an electron from the radical amine species and then take up a proton. This results in the formation of the original molecule of the protonated amine and benzyl hydroperoxide. In the second possible pathway the peroxide radical eliminates a hydrogen atom from the toluene molecule, and reaction proceeds as a chain radical process [17, 18]. As is well known, a hydroperoxide can readily be converted into a carbonyl compound. Light, and the presence of metal ions, accelerate this transformation.

It is necessary to find an explanation of the fact that only biphenyls with nitrogen atoms in the  $\alpha$  positions show appreciable activity. It may be supposed that in the photooxidation a form of phenanthroline that is protonated only on one nitrogen atom is active. The second nitrogen atom may then act as a base and take up the proton eliminated from the toluene radical cation. Since the electron from toluene is transferred to the ring containing the protonated nitrogen atom, the second nitrogen atom, which acts as a base, must be disposed at a fairly short distance from the protonated nitrogen atom. This requirement is probably not satisfied by the nitrogen atoms in 4,4'-bipyridine, which are at a considerable distance from one another. The acceptance of a proton by the basic nitrogen atom favors a shift in the equilibrium (1) to the right.



It should be noted that a triphenylpyrylium salt, in which the positive charge is concentrated on the oxygen atom, was used recently as a photosensitizer in the oxidation of alkenes [7].

We can also suppose the possibility of simultaneous activation at the two nitrogen atoms of phenanthroline or 2,2'-bipyridine for molecules of toluene and dioxygen (2). The immediately formed benzyl radical and superoxide radical anion, which are close in space, recombine, giving a peroxide anion which can accept a proton from the solvent.



In the irradiation of a solution of toluene in presence of  $\text{FeCl}_3$ , there probably occurs, at the first stage, the excitation of the  $\text{Fe(III)}$  compound. Further reaction may take two courses: After the transfer of an electron from toluene the toluene radical cation and an  $\text{Fe(II)}$  derivative are formed, or in the excited  $\text{FeCl}_3$  species the transfer of an electron from the chloride ligand to  $\text{Fe(III)}$  occurs, resulting in the formation of a  $\text{Cl}^\cdot$  radical and  $\text{Fe(II)}$ . The  $\text{Cl}^\cdot$  radical may react with toluene, giving a benzyl radical. Thus, in both courses a benzyl radical is formed, and further reaction proceeds by a chain radical process. Since  $\text{Fe(II)}$  may be oxidized slowly by molecular oxygen into  $\text{Fe(III)}$ , the iron salt acts as a catalyst initiating the reaction. Less understandable is the accelerating action of  $\text{FeCl}_3$  when used simultaneously with phenanthroline. It may be supposed that in this case the active species is a complex of  $\text{FeCl}_3$  with the protonated form of phenanthroline, and it is possible that the central ring participates in the complex formation, for in the case of 2,2'-bipyridine the addition of  $\text{FeCl}_3$  does not lead to increase in the reaction rate.

#### EXPERIMENTAL

The irradiation of samples of the solutions was conducted with the light from a DRSh-1000 high-pressure mercury lamp (1000 W) in a glass vessel or with a medium-pressure mercury lamp (125 W) in a quartz vessel. The vessels had jackets, through which cooling water ( $10 \pm 2^\circ\text{C}$ ) was passed; the solutions were agitated vigorously with a magnetic stirrer. In the experiments we used solutions of the photocatalysts in a mixture of 1.0 ml of  $\text{H}_2\text{O}$ , 4.5 ml of  $\text{CH}_3\text{-COOH}$ , and 0.5 ml of toluene. After the irradiation an equal volume of water was added to the solution, the mixture was extracted with three 2-ml portions of chloroform, and the extract was washed with water and  $\text{NaHCO}_3$  solution and was dried with  $\text{Na}_2\text{SO}_4$ . A definite part of the solution was applied to a Silufol UV-254 plate, and elution was effected with a 2:1 mixture of hexane and chloroform. The benzaldehyde band was cut out and washed with 3 ml of chloroform, and the amount of benzaldehyde was determined by its absorption in UV (Specord UV-Vis spectrophotometer). The competing-oxidation reactions were conducted as described earlier [19].

The work was carried out in implementation of the scheme for the cooperation of the academies of sciences of socialist countries in the field of catalysis.

#### CONCLUSIONS

The irradiation of a solution of toluene in acetic acid in presence of catalytic amounts of 1,10-phenanthroline or 2,2'-bipyridine leads to the oxidation of toluene to benzaldehyde by the dissolved oxygen. An addition of  $\text{FeCl}_3$  raises the rate of the oxidation process.

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