

## OXIDATION OF BENZALDEHYDE BY DIOXYGEN. PHOTOINITIATED REACTION

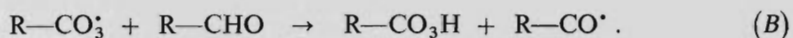
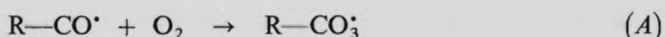
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The photoinitiated oxidation of benzaldehyde is catalyzed by traces of transition metal ions. The photocatalytic effects of transition metals are explained in terms of the formation of their unstable oxidation states which act as catalysts of the thermal oxidation. The reaction catalyzed by Fe(II) and Fe(III) ions is discussed in detail.

The first quantitative study of the photoinitiated oxidation of benzaldehyde by dioxygen, reported by Bäckström<sup>1</sup>, revealed high quantum yields of the reaction ( $\phi \gg 1$ ). In view of this observation, the reaction was considered to proceed by a radical chain mechanism<sup>2</sup>. Although the mechanism has been modified several times in details<sup>3-7</sup>, it has always been assumed to involve, in the first step, the formation of the radical R—CO• which initiates the propagation reactions (A) and (B):



The reaction has been considered to be terminated by radical recombinations or by reactions of the radicals with inhibitors<sup>1-7</sup>.

Since the oxidation of benzaldehyde has some characteristic features (high quantum yields, inhibition by alcohols) in common with the oxidation of sulphite, the two reactions were studied in parallel<sup>1,8</sup>. Recently it had been demonstrated<sup>9,10</sup> that a prerequisite for the photoinitiated oxidation of sulphite to occur is that traces of transition metal ions be present in the solution, and that the concentration of the photocatalytically active ions determines the quantum yield of the reaction. In this context, the question arises whether transition metal ions affect also the photoinitiated oxidation of benzaldehyde, and if so, whether the mechanism of their action is similar.

## EXPERIMENTAL

Prior to use, analytical grade benzaldehyde (Reachim) was doubly vacuum distilled and then vacuum rectified. The purity of so obtained benzaldehyde was checked by measuring the rate of its thermal oxidation by dioxygen<sup>11</sup>. The preparation of acetylacetonates and ethyl caproates of transition metals, which were used as catalysts, has been described or cited in a previous paper<sup>11</sup>. Benzene (Lachema) and cyclohexane (International Enzymes Ltd.) of analytical grade were used as solvents.

*Procedure.* The photoinitiated oxidation of benzaldehyde by dioxygen was carried out in a thermostatted quartz vessel connected to a gas burette filled with oxygen. The quartz vessel was vigorously shaken. As a light source we used a HBO 500 W high-pressure mercury arc placed in an aluminium cooling block which ensured moderate constant cooling, and thereby a constant light flux. Since the main attention was paid to the study of photocatalytic effects of transition metal ions which catalyze also the thermal reaction, it was desirable to maintain the light flux, and thereby the ratio of the rates of photoinitiated and thermal reactions, as great as possible. For this reason, the initiating radiation was passed mostly unfiltered. In experiment with FeCl<sub>3</sub> additions in which quantum yields were measured, the initiating radiation was monochromatized by means of a IF 350 interference filter (Carl Zeiss, Jena) which transmitted the following lines of the mercury arc: 313 nm (7%), 334 nm (16%), and 365 nm (3%). The parenthesized percentages indicate the transmittance of the IF 350 interference filter for the specified wavelengths. The course of the benzaldehyde oxidation was followed by measuring the volume of consumed oxygen.

Another experimental arrangement used for following the course of the reaction by way of determining the concentrations of benzoic and peroxobenzoic acids has been described in our previous paper<sup>12</sup>.

The effect of the initiating radiation on the interaction between the catalysts and benzaldehyde was examined by means of the spectrophotometric and EPR methods. The electronic absorption spectra were taken on a SP 800 B spectrophotometer (Unicam, Cambridge). The formation of Fe(II) was proved by reaction with *o*-phenanthroline and by subsequent measurement of the corresponding absorption maximum at 510 nm (ref.<sup>13</sup>).

The EPR spectra were measured on a JES-3B instrument (JEOL, Japan) working in the X-band, modulation frequency 100 kHz, microwave power up to 15 mW. The measurements were made on samples placed in quartz cells at the ambient temperature and at 103 K. Mn(II) JEOL and carbon were used as standards. The irradiation was carried out in a resonator by means of a HBO 200 W arc (Narva, Berlin).

The intensity of the initiating radiation was measured by the classical method using a ferrioxalate actinometer<sup>13</sup>.

The experimental data were processed on a Hewlett-Packard 9830 A computer. The data were fitted to polynomials using the regression method, and the mean relative deviations were evaluated.

## RESULTS AND DISCUSSION

The quantitative, and often even the qualitative, interpretation of experimental data on photoinitiated reaction of dioxygen is always a matter of some difficulty. The photoinitiated oxidation is inevitably accompanied by the thermal reaction. If data on pure photochemical reaction are to be obtained, a correction must be applied for the thermal process. In the previously studied oxidation of sulphite, the determination was mostly restricted to the initial rate of photochemical reaction which was

obtained as the difference between the initial rate at irradiation and the rate of the thermal reaction just before admission of light to the reaction system. This approach could not be applied in the case of photooxidation of benzaldehyde because of the autocatalytic character of the reaction and occasional marked changes observed in the reaction course. The thermal and photoinitiated reaction were therefore followed in parallel on the same solutions of the same "age". The rate of the photochemical reaction was calculated by subtracting the rate of the thermal reaction from the overall rate at irradiation. Because of the inevitable scatter in the data on the thermal trace-catalyzed reaction, the rate of the photochemical reaction can be determined in the above described way only if it is higher than the rate of the thermal reaction; the higher the proportion of the thermal reaction in the overall rate at irradiation, the lower the reliability of the value obtained for the rate of the photochemical reaction. In our experiments, the rate of the thermal reaction did not exceed 30% of the overall rate at irradiation.

In the first works<sup>1,2</sup>, which laid the foundation of the nowadays generally accepted radical mechanism of dioxygen reactions, pure (100%) benzaldehyde was oxidized, and the photoinitiated reaction was initiated by light of 254 nm and 265 nm wavelengths. At these wavelengths, the absorption coefficient of benzaldehyde has values of  $5.5 \text{ m} \cdot 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$  and  $7.5 \cdot 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ , respectively. From the Lambert-Beer law it follows that more than 99% of the initiating radiation of 254 nm wavelength is absorbed by a layer of pure benzaldehyde of as little as  $5 \cdot 10^{-5} \text{ cm}$  thickness. For 265 nm, the layer which will absorb the same amount of light is  $3 \cdot 10^{-4} \text{ cm}$  thick. Hence it is evident that in the above cited experiments only a very thin surface layer of the reaction system was affected by the initiating light. Similar situation is found in recent works. André and coworkers<sup>6</sup>, for example, used light of 313 nm wavelength to initiate oxidation of benzaldehyde; in this case a layer of  $8 \cdot 10^{-3} \text{ cm}$  thickness will absorb 99% of the radiation. Fig. 1 shows a plot of the amount of absorbed light against the thickness of absorbing layer for the wavelengths applied in the discussed papers<sup>1,2,5,6</sup>. Since the influence of light of the wavelengths 254 nm, 265 nm, and 313 nm on the oxidation rate has been conclusively proved<sup>1,2,5,6</sup>, it must be concluded that in the surface layer a particle is photochemically generated which is sufficiently long-lived to survive the transport from the irradiated layer into the bulk of the reaction solution. According to the classical concept of the reaction, this particle may be either an excited triplet  $T_1$  or a product of its decay, namely the radical  $\text{C}_6\text{H}_5\text{CHO}^*$  (ref.<sup>5,6</sup>). The half-life of  $T_1$  in pure benzaldehyde at 18°C was evaluated by Bäckström and Riiner<sup>5</sup> as  $3 \cdot 10^{-9} \text{ s}$ . This time is obviously too short for the triplet state to occur beyond the irradiated microlayer. On the other hand, the transport of the  $\text{C}_6\text{H}_5\text{CHO}^*$  radicals from the irradiated layer into the bulk of the reaction liquid followed by the propagation reaction (A) cannot be ruled out. Yet, in view of the small volume of the irradiated microlayer in which all the initiating light is absorbed, it may be assumed that the radicals

would be formed in high concentration resulting necessarily in their recombination. However, no products of radical recombination have been observed. A more probable alternative to the formation of the initiating radical seems to be the photochemical generation of a catalyst of thermal reaction, *i.e.*, the photochemical reduction of trace metals to the form which catalyzes the thermal oxidation of benzaldehyde (*e.g.*, photoreduction of Fe(III) to Fe(II), see below). The conditions in the irradiated microlayer are all in favour of the photochemical reduction: high absorption of light in the small volume results in removal of oxygen, producing anaerobic conditions; there is abundant supply of energy, and high concentration of a strong reducing agent – the excited benzaldehyde.

The catalytic effects of transition metals on the photoinitiated oxidation must be studied simultaneously with the catalytic effects on the thermal reaction. In our previous paper<sup>11</sup> we described the catalytic effects of transition metal ions on the thermal reaction, and discussed the causes of the low reproducibility of observations. In the present study, we found that one of these causes is the “ageing” of the stock solution. The “ageing” manifests itself by an induction period in the kinetic course of the reaction catalyzed by (2,4-pentanedionato)Fe(III) complex,  $[\text{Fe}(\text{acac})_3]$ . With the “aged” benzaldehyde solutions, the catalytic effect of  $[\text{Fe}(\text{acac})_3]$  strongly depends

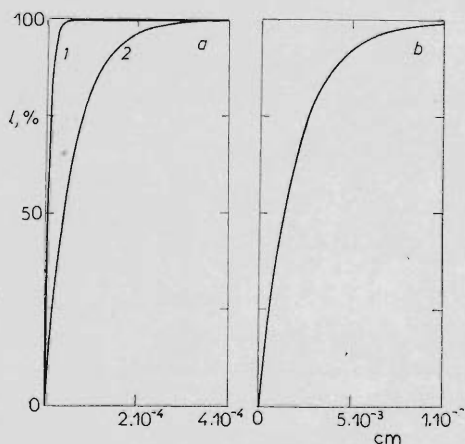


FIG. 1

Plot of the absorbed light in % vs the thickness of the absorbing layer: *a* Bäckström<sup>1,2</sup>; 1 254 nm, 2 265 nm; *b* André and coworkers<sup>6</sup>; Bäckström and Riiner<sup>5</sup>; initiating radiation – 313 nm; *l* the amount of absorbed light

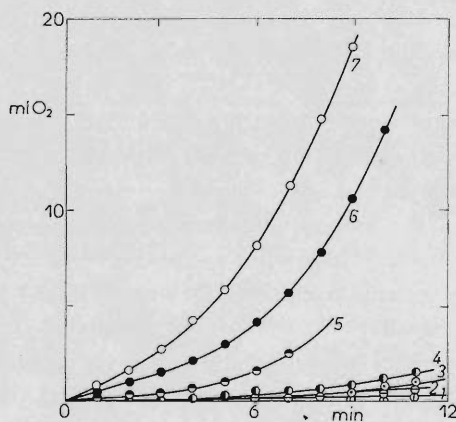


FIG. 2

Effect of the “age” of benzene solution of benzaldehyde containing  $[\text{Fe}(\text{acac})_3]$  on the rate of thermal oxidation.  $[\text{C}_6\text{H}_5\text{CHO}]_0 = 0.5 \text{ mol dm}^{-3}$ ;  $[\text{Fe}(\text{acac})_3] = 1 \cdot 10^{-5} \text{ mol dm}^{-3}$ ;  $[\text{O}_2] = \text{sat.}$ ; times of standing: 1–4  $\leq 120 \text{ s}$ ; 5 180 s; 6 1 020 s; 7 3 600 s

on the time for which the solution of benzaldehyde with  $[\text{Fe}(\text{acac})_3]$  is allowed to stand before starting the reaction, *i.e.*, before saturating the solution with oxygen. The dependence is represented in Fig. 2 which shows that the longer the standing of  $[\text{Fe}(\text{acac})_3]$  with the benzaldehyde solution, the higher the rate of benzaldehyde oxidation after starting the reaction by saturation of the reaction solution with oxygen. Since it has been proved<sup>11</sup> that the effect benzaldehyde has on  $[\text{Fe}(\text{acac})_3]$  is to reduce Fe(III) to Fe(II) which has a markedly higher catalytic activity, the dependence represented in Fig. 2 may be interpreted in terms of generation of catalytically more active Fe(II) from the catalytically less active Fe(III). The fact that the dependence is most pronounced with "aged" solutions may be explained as follows. The "ageing" essentially means formation of inhibitors of the oxidation. The higher the background level of inhibitors, the higher the catalyst (here Fe(II)) concentration necessary to start the reaction, and the longer the time required for building up a sufficient concentration of the catalyst. The formation of catalyst (Fe(II)) is also suggested by the autocatalytic course of the process. However, the

TABLE I

Effect of  $\text{FeCl}_3$  additions ( $\text{mol dm}^{-3}$ ) on the quantum yields of photoinitiated oxidation of benzaldehyde by dioxygen;  $[\text{C}_6\text{H}_5\text{CHO}]_0 = 0.5 \text{ mol dm}^{-3}$ ;  $[\text{O}_2] = \text{sat.}$ ;  $20^\circ\text{C}$

Time min	$\text{FeCl}_3$ addition					
	0	$9.1 \cdot 10^{-7}$	0	$4.8 \cdot 10^{-6}$	0	$9.1 \cdot 10^{-6}$
	Quantum yield $\cdot 10^{-2}$ (molecules $\text{O}_2/h\nu$ )					
1	0.6	0.6	0.7	1.6	0.7	0.9
2	0.7	1.0	0.9	3.5	1.0	4.5
3	1.0	1.2	1.0	4.2	1.1	6.5
4	1.0	1.5	1.0	4.3	1.2	5.8
5	1.0	1.7	1.0	3.7	1.2	5.0
6	1.2	1.5	1.2	3.7	1.3	4.6
7	1.1	1.3	1.1	2.6	1.2	3.9
8	1.1	1.4	1.1	2.7	1.2	3.5
9	1.1	1.3	1.1	2.6	2.7	3.1
10	1.0	1.2	1.0	2.3	1.1	2.8
11	1.0	1.3	1.0	2.1	1.1	2.6
12	0.9	1.2	1.0	2.0	1.0	2.3
13	1.0	1.3	0.9	1.8	1.0	2.0
14	0.9	1.0	1.0	1.8	1.0	—
15	1.0	1.0	0.9	1.5	0.9	—

latter might also be due to induced oxidation of background inhibiting impurities, or, in line with the current interpretation<sup>14,15</sup> of autocatalysis, to the initiation by peroxocompounds formed, in our case peroxobenzoic acid. Because of limited concentration of the stock solutions, additions of  $1 \cdot 10^{-2} \text{ mol dm}^{-3}$  peroxobenzoic acid and  $5 \cdot 10^{-2} \text{ mol dm}^{-3}$  dibenzoyl peroxide were only tested. No effects of additions of these compounds on the rate of benzaldehyde photooxidation were detected.

Similarly as in the case of sulphite oxidation<sup>9,10</sup>, it has been found for the photo-initiated oxidation of benzaldehyde that additions of transition metal compounds enhance the rate and the quantum yields of the reaction. The catalytic effect has been conclusively proved for additions of  $[\text{Fe}(\text{acac})_3]$ ,  $\text{FeCl}_3$ , manganese(II) ethyl caproate, chromium(III) ethyl caproate, and  $[\text{Cr}(\text{acac})_3]$ . A part of the experimental results concerning photocatalytic effects of manganese(II) and chromium(III) ethyl caproates in cyclohexane solutions have been reported in a previous communication<sup>12</sup>. Fig. 3

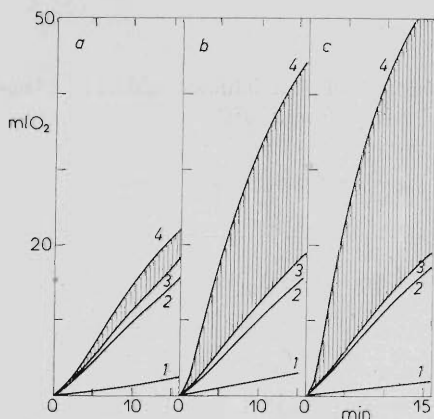


FIG. 3

Photocatalytic effect of  $\text{FeCl}_3$ .  $[\text{FeCl}_3]$  additions: *a*  $9 \cdot 1 \cdot 10^{-7} \text{ mol dm}^{-3}$ ; *b*  $4 \cdot 8 \cdot 10^{-6} \text{ mol dm}^{-3}$ ; *c*  $9 \cdot 1 \cdot 10^{-6} \text{ mol dm}^{-3}$ ; 1 thermal reaction, addition of  $\text{FeCl}_3$ , 2 photo-initiated reaction, no  $\text{FeCl}_3$ , 3 sum of 1 and 2, 4 photo-initiated reaction, addition of  $\text{FeCl}_3$ . The shaded area (difference between 4 and 3) represents the increase due to the photocatalytic effect of  $\text{FeCl}_3$ .  $[\text{C}_6\text{H}_5\text{CHO}]_0 = 0 \cdot 5 \text{ mol dm}^{-3}$ ; benzene solution;  $20^\circ\text{C}$  initiated with a HBO 500 arc with a IF 350 filter

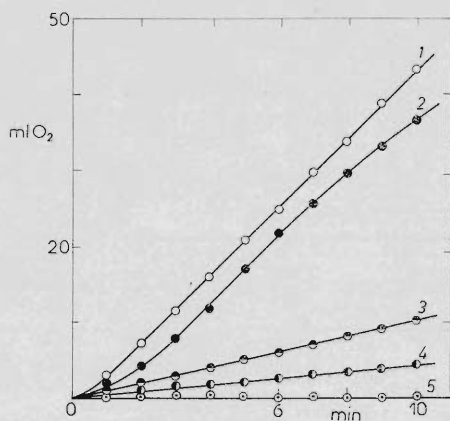


FIG. 4

Effect of acetylacetone on the photo-initiated oxidation of benzaldehyde by dioxygen.  $[\text{C}_6\text{H}_5\text{CHO}]_0 = 0 \cdot 42 \text{ mol dm}^{-3}$ ;  $[\text{Fe}(\text{acac})_3] = 8 \cdot 3 \cdot 10^{-5} \text{ mol dm}^{-3}$ ; HBO 500 arc;  $20^\circ\text{C}$ ;  $[\text{O}_2] = \text{sat.}$ ; acetylacetone additions: 1 0; 2  $8 \cdot 3 \cdot 10^{-5} \text{ mol dm}^{-3}$ ; 3  $4 \cdot 2 \cdot 10^{-2} \text{ mol dm}^{-3}$ ; 4  $8 \cdot 3 \cdot 10^{-2} \text{ mol dm}^{-3}$ ; 5  $0 \cdot 81 \text{ mol dm}^{-3}$

illustrates the catalytic effect of  $\text{FeCl}_3$  additions on the photochemical oxidation of benzaldehyde in benzene solution (IF 350 nm filter). Table I gives the relevant values of quantum yields. Because the rate of photochemical oxidation varied in the course of the reaction, each quantum yield was calculated from the average rate between two consecutive measurements.

In the study of the photochemical oxidation of sulphite it was found that on addition of complexing agents the reaction was retarded and finally stopped, depending on the concentration of the added complexing agent<sup>9</sup>. On the basis of this observation, the hypothesis was propounded that no photoinitiated oxidation of sulphite would occur in complete absence of transition metal ions<sup>14</sup>. It was of interest to test whether addition of an agent which forms complexes with transition metals would result in a decrease in the rate of the photoinitiated oxidation of benzaldehyde. Acetylacetone was selected as the complexing agent. The results obtained are shown in Fig. 4. Just as in the case of the thermal reaction<sup>11</sup>, additions of acetylacetone to the reaction solution retard and eventually stop the oxidation of benzaldehyde. If we consider the finding of the positive influence of additions of transition metals in conjunction with the observation of the inhibiting effect of complexing agent additions, we can advance the hypothesis that the presence of the catalyzing transition metal ions is a prerequisite for the operation of both the thermal and photoinitiated reactions. In other words, as the concentration of transition metal ions in the reaction system approaches zero, so does the rate, and consequently also the quantum yield, of the photoinitiated oxidation of benzaldehyde.

In order to elucidate the mechanism, we studied changes in the oxidation state of iron in the catalyst on exposure to benzaldehyde and to the initiating radiation. The EPR spectra showed that on irradiation of oxygen-free solution of iron(III) chloride in benzaldehyde by UV light, the singlet EPR signal due to  $\text{Fe(III)}$  ( $g = 2.0128$ ;  $H_{\text{pp}} = 9.20$  mT; PP = peak to peak) gradually vanishes (Fig. 5). In view of the results of electronic absorption spectra studies and of the proof of  $\text{Fe(II)}$  formation by means of *o*-phenanthroline (see below), the disappearance of the EPR signal due to  $\text{Fe(III)}$  may be unequivocally ascribed to the reduction of  $\text{Fe(III)}$  to  $\text{Fe(II)}$ . Once the photoreduction has occurred, the singlet EPR signal can only be restored by bubbling the solution with oxygen.

In subsequent measurements, changes in EPR signal were followed over long-term periods for  $\text{FeCl}_3$  in benzaldehyde. The solution was not irradiated by UV light, and thus the thermal reduction of  $\text{FeCl}_3$  by benzaldehyde was only involved. In keeping with the results of studies on electronic absorption spectra, no thermal reduction of  $\text{FeCl}_3$  by benzaldehyde was found to occur. The original intensity of the EPR signal due to  $\text{Fe(III)}$  remained constant over a period of two months. The only observable change was a slight broadening of the singlet signal during the first 48 hours, corresponding probably to changes in the  $\text{Fe(III)}$  ligand field.

TABLE II

Effect of Tinuvine on the rate of photochemical oxidation of benzaldehyde by dioxygen catalyzed by chromium(III) ethyl caproate.  $[C_6H_5CHO]_0 = 3.4 \text{ mol dm}^{-3}$ ;  $[Cr(III) \text{ ethyl caproate}] = 8.6 \cdot 10^{-4} \text{ mol dm}^{-3}$ ;  $[O_2] = \text{sat.}$ ; cyclohexane solutions; irradiated by the entire spectrum of HBO 500 W arc; *a* no addition; *b* Tinuvine addition of  $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ . The product concentrations are those built up by photochemical reaction ("photoconcentrations"), and were obtained as differences between the overall analytical concentrations after irradiation and the concentrations built up by thermal reaction.

Time min	Benzoic acid		Peroxybenzoic acid	
	<i>a</i>	<i>b</i>	<i>a</i>	<i>b</i>
5	0.035	0.020	0.030	0.003
10	0.067	0.024	0.044	0.005
15	0.119	—	0.069	0.007
20	0.203	0.037	—	0.010
25	0.259	—	0.085	—
30	—	0.042	—	0.012

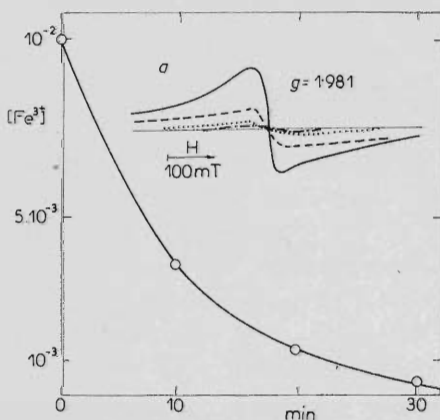


FIG. 5

Effect of irradiation of benzaldehyde- $FeCl_3$  mixture by UV light in the absence of air on  $Fe(III)$  concentration. EPR signal due to  $Fe(III)$  as a function of time: — 0 min; - - - 10 min, ····· 20 min, - · - · - 30 min. 103 K; HBO 200 arc;  $[Fe(III)]_0 = 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$

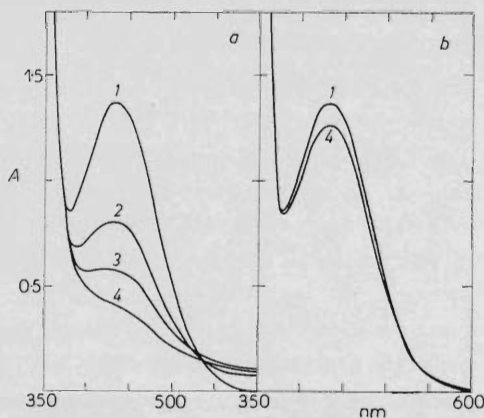


FIG. 6

Absorption spectra.  $4 \cdot 10^{-4} \text{ mol dm}^{-3} [Fe \cdot (acac)_3] + 5 \cdot 10^{-2} \text{ mol dm}^{-3} C_6H_5CHO$  in benzene;  $20^\circ C$ ; cell 1 cm; time: 1 immediately after mixing; 2 10 min; 3 20 min; 4 30 min; *a* unfiltered light of HBO 500 arc; *b* no irradiation (thermal reaction)



In the paper on the thermal oxidation of benzaldehyde<sup>11</sup> it was shown that  $[\text{Fe}(\text{acac})_3]$  is thermally reduced by benzaldehyde, and that an excess of acetylacetone would retard or even stop the reduction of Fe(III) in  $[\text{Fe}(\text{acac})_3]$ . In the present work we studied changes of the oxidation state of iron by means of electronic absorption spectroscopy and by using an EPR spectrophotometer. Both measurements indicated that the UV light substantially accelerates the reduction of Fe(III) in  $[\text{Fe}(\text{acac})_3]$  by benzaldehyde. The influence of UV radiation is most pronounced in dilute solutions ( $[\text{Fe}(\text{acac})_3] \leq 1 \cdot 10^{-2} \text{ mol dm}^{-3}$ ) where the thermal reaction proceeds more slowly. Typical patterns of variations in the electronic absorption spectra for irradiated and unirradiated solutions are shown in Fig. 6.

Further studies have shown that the photochemical reduction of Fe(III) is inhibited by the same substances that inhibit the photooxidation of benzaldehyde. The inhibiting effect has been proved for acetylacetone,  $\alpha$ -naphthol, diphenylamine, and Tinuvin 770 (bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate). The inhibiting effect of Tinuvin on the photoinitiated oxidation of benzaldehyde is documented in Table II; the effect of Tinuvin on the thermal and the photoinitiated reduction of Fe(III) in  $[\text{Fe}(\text{acac})_3]$  by benzaldehyde is illustrated in Fig. 7.

In the previous paper<sup>11</sup> it was shown that under certain conditions no catalytic effect is produced by an addition of  $\text{FeCl}_3$  to benzaldehyde solution, and that the reaction is only started when the reaction mixture containing  $\text{FeCl}_3$  is irradiated. It was therefore of interest to examine whether light would bring about photochemical reduction of Fe(III) in  $\text{FeCl}_3$  to Fe(II). In addition to the above mentioned EPR studies, the examination was conducted also spectrophotometrically, with the aim of proving (or ruling out) the formation of Fe(II). The spectrophotometric studies confirmed the EPR finding that  $\text{FeCl}_3$  is not thermally reduced by benzaldehyde.

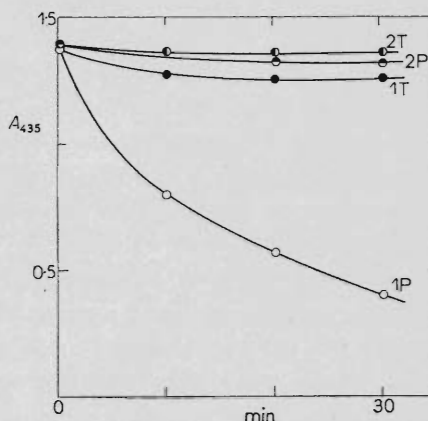


FIG. 7

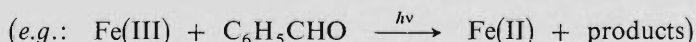
Thermal and photoinitiated reduction of  $[\text{Fe}(\text{acac})_3]$  in benzene solution. Absorbance at 435 nm ( $\lambda_{\text{max}}[\text{Fe}(\text{acac})_3]$ ) vs time.  $[\text{Fe}(\text{acac})_3]_0 = 4 \cdot 10^{-4} \text{ mol dm}^{-3}$ ;  $[\text{C}_6\text{H}_5\text{CHO}]_0 = 5 \cdot 10^{-2} \text{ mol dm}^{-3}$ ;  $20^\circ\text{C}$ , inert atmosphere; 1 cm cell; T = thermal reaction; P = photoinitiated reaction (entire spectrum of HBO 500 arc). 1 no addition; 2 [Tinuvin] =  $1 \cdot 10^{-3} \text{ mol dm}^{-3}$

Moreover, the photochemical formation of Fe(II) was unambiguously proved by identifying the Fe(II)-*o*-phenanthroline complex which showed a typical absorption maximum at 510 nm.

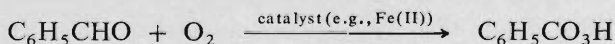
### Reaction Mechanism

The mechanism of benzaldehyde oxidation presented in the literature<sup>1-8</sup> was proposed on the basis of the observed high quantum yields of the photoinitiated reaction. In this paper, it has been shown that the magnitude of the quantum yield is affected, and essentially determined, by the concentration of the catalyzing transition metal ions. On exposure to light, metal ions in lower oxidation states are formed which effectively catalyze the thermal reaction. Another fact which supports the conclusion that the effect of light is to generate photochemically a catalyst of thermal reaction is the finding that substances inhibiting the photochemical oxidation of benzaldehyde (acetylacetone,  $\alpha$ -naphthol, Tinuvine) inhibit also the photochemical reduction of Fe(III) to Fe(II). On the basis of these observations, considering also the fact that the reaction can be initiated by radiation absorbed in a surface micro-layer, the following mechanism for the photoinitiated oxidation of benzaldehyde is proposed:

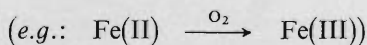
Initiation = photochemical formation of catalyst of thermal reaction



Propagation = catalyzed oxidation of benzaldehyde



Termination = catalyst deactivation



It is evident from the reaction scheme that the proposed mechanism is formally an analogy of the radical chain mechanism. However, the high quantum yields do not arise as a result of radical chain reaction, but as a consequence of the catalyzing action of transition metal ions in unstable oxidation states generated by photoinitiated reduction of stable, catalytically inactive or poorly active metal ions by benzaldehyde. For the time being, insufficient experimental data are available for a detailed discussion of the individual steps of this complex reaction. The finding that the high quantum yields of the photoinitiated oxidation of benzaldehyde are due to the catalytic cycles, and not to a radical chain mechanism, has corroborated for another system<sup>14</sup> that high quantum yields of a photoinitiated reaction cannot be considered as evidence for the radical chain mechanism.

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