

OXIDATION OF BENZALDEHYDE BY DIOXYGEN. THE THERMAL REACTION

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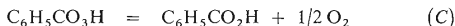
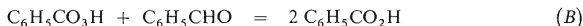
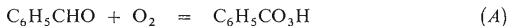
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The oxidation of benzaldehyde is catalyzed by transition metal ions even when these are present in trace concentrations. In complete absence of the ions, the reaction between benzaldehyde and dioxygen would not take place.

A study has been made of the oxidation of benzaldehyde in benzene catalyzed by transition metal complexes. The catalytic activity of transition metals is higher when they assume their lower oxidation states. When the reaction is catalyzed by iron(III) bis(2,4-pentanedionato)-complex, the first reaction step is the reduction of Fe(III) to Fe(II), the latter being the catalyst of the thermal reaction. The mechanism proposed for the catalyzed reaction does not involve free radical formation.

Autoxidation of benzaldehyde¹ and autoxidation of sulphite² were the first two reactions of dioxygen to be interpreted in terms of the free radical chain mechanism. The classical concept of the mechanism of these reactions was developed when little was known about the effect of metal ions in trace concentrations on the thermal and photochemical reactions. New findings regarding the mechanism of sulphite oxidation³ gave us an impetus to re-investigate the thermal and photochemical reactions of benzaldehyde.

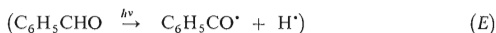
Most authors⁴⁻⁶ share the view that the oxidation of benzaldehyde may be represented by the following reaction scheme:



The first step involves the formation of peroxobenzoic acid which has been proved conclusively to be an intermediate of the reaction. A further intermediate has been assumed to be an association product of peroxobenzoic acid and benzaldehyde⁷; however, no definite evidence has so far been given for its presence in the reaction system. Few authors have dealt in detail with what is going on with the peroxobenzoic

acid, and the extent to which the reactions of peroxobenzoic acid (equations (B) and (C)) contribute to benzoic acid formation is unclear. The main attention has been focused on the initial stage of the reaction, *i.e.* on the formation of peroxobenzoic acid. In view of high quantum yields observed for the photoinitiated reaction, and the established catalytic effect of metal ions on the thermal reaction, the reaction of benzaldehyde with dioxygen has been interpreted⁴⁻⁶ in terms of the free radical chain mechanism. The most frequently quoted variant of this mechanism is represented by the following reaction scheme:

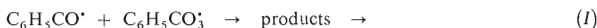
Initiation:



Propagation:



Termination:



In this work we report results of our studies on the thermal reaction, and discuss both the so-called non-catalyzed reaction and the reaction catalyzed by metal complexes. The main objective of the study was to elucidate the mechanism of the initiating step of the thermal reaction.

EXPERIMENTAL

Chemicals

Benzaldehyde (Reachim, USSR) was purified by repeated vacuum distillation followed by double rectification on a 1 m long packed column. Both the distillation and the rectification were carried out in an atmosphere of completely deoxygenated nitrogen. The effectiveness of the purifying operations was checked by following the consumption of oxygen during non-catalyzed oxidation of 100% benzaldehyde. So obtained benzaldehyde was stored under nitrogen in sealed glass ampoules placed in the dark. Activation analysis established that the benzaldehyde contained $2 \cdot 10^{-7} \text{ mol dm}^{-3}$ of manganese.

The peroxobenzoic acid was prepared from dibenzoylperoxide and sodium ethoxide following the method of Braun⁸. The concentration of the active component in benzene solution was determined iodometrically. Transition metal 2,4-pentanedionates (acetylacetonates) and ethylcaproates, and in some experiments also commercial $\text{Fe}(\text{H}_2\text{O})_6\text{Cl}_3$ and $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ (Lachema, Brno), were used as catalysts. The Mn(III), Co(II), Co(III), Cr(III) and Ni(II) acetylacetonates were prepared according to ref.⁹. The Fe(III) acetylacetonate was commercial product (E. Merck). The Fe(II), Co(III), Mn(III), Cr(III), Ni(II) and Cu(II) ethylcaproates were prepared as described in ref.¹⁰.

Analytical grade benzene (Lachema, Brno) was used as solvent in the kinetic experiments, while spectroscopic grade benzene (E. Merck) was employed in the spectrophotometric measurements.

Nitrogen was freed from traces of oxygen by passing it through a series of washing bottles with a chromium(II) salt. Oxygen was used without further purification.

Procedure

The reaction of benzaldehyde with oxygen was followed volumetrically. The apparatus consisted of a thermostatted reaction vessel placed in a light-tight box, and connected through its capillary entry to a gas burette. The reaction vessel was vigorously shaken; the frequency of shaking was changed to check whether the reaction proceeded in the kinetic region. Both the reaction vessel and the gas burette were thermostatted at 25°C.

When studying the catalyzed reaction, 10 ml of 0.5 mol dm^{-3} benzaldehyde was first oxidized for 300 s without an addition of catalyst. This permitted to eliminate the runs where an increased amount of trace impurities affected the course of the non-catalyzed reaction. The course of the catalyzed reaction was followed till an amount of oxygen had been consumed corresponding theoretically to the oxidation of 20% of benzaldehyde to peroxobenzoic acid. At the end of each run the peroxobenzoic acid content and benzoic acid content were determined in the reaction mixture.

The "non-catalyzed" reaction was studied using either 10 ml of 100% benzaldehyde or 10 ml of 0.5 mol dm^{-3} benzaldehyde in either of the solvents used.

The interactions between the catalyzing complexes and benzaldehyde in the absence of oxygen were followed spectrophotometrically (Specord UV-VIS, Zeiss Jena). Absorption spectra were recorded at wavelengths ranging from 300 to 800 nm. When working under oxygen-free conditions, the catalyst solution was bubbled with nitrogen in the cell sealed with a silicon-rubber stopper carrying a syringe needle through which the inert gas was supplied. Other components (benzaldehyde, inhibitor), freed of oxygen before use by bubbling with nitrogen, were also introduced into the solution through the needle.

Analytical

The concentration of peroxobenzoic acid in the benzene solution was determined by iodometric titration. The total acidity was determined alkalimetrically (0.1 mol dm^{-3} -KOH) using phenolphthalein as indicator. The benzoic acid content was calculated as the difference between the two determinations.

Fe(II) was identified by reaction with *o*-phenanthroline as described by Hatchard and Parker¹¹.

RESULTS AND DISCUSSION

"Non-Catalyzed Reaction"

In the literature^{4,12-16} one finds conflicting data on the course of the non-catalyzed reaction which are difficult to assess. Our experiments have led to the following conclusions: 1) The course of the oxidation of benzaldehyde is affected to a considerable extent by sunlight. Therefore, unbiased data on the course of the thermal reaction can only be obtained if the reaction proceeds in the absence of light. 2) The oxidation of benzaldehyde is catalyzed by transition metal compounds. The catalytic effects are very pronounced even at subanalytical concentrations of the metals in the reaction system. 3) Nucleophilic species inhibit the oxidation of benzaldehyde. The inhibiting effects are very large even when the nucleophilic species are present in subanalytical concentrations in the reaction system.

The results obtained in the study of the "non-catalyzed reaction" have led us to adopt the hypothesis that the thermal reaction between benzaldehyde and dioxygen would not occur if transition metals were completely absent from the reaction system. (Kuhn and Meyer¹⁵ have stated that extremely pure benzaldehyde gives no reaction with dioxygen.) However, in real systems, which always contain traces of metals, the oxidation proceeds at a measurable rate. Nucleophilic species present in the reaction system as impurities form association products with metal ions, thus inducing their catalytic activity.

It is evident that all the literature data on the non-catalyzed reaction are erratic. The reaction courses as described in individual papers depended on levels of impurities in the reaction system, and we see no point in attempting to interpret them.

Catalyzed Reaction

To obtain information on the oxidation of benzaldehyde under well-defined conditions, we studied the course of the reaction catalyzed by metal salts and metal complexes.

It has been found that the course of the catalyzed reaction depends to a marked extent on the nature of the catalyzing metal and on the type of the ligand. The nature of the catalyst influences markedly not only the reaction rate, but also the relative proportions of the products. Table I gives the ratio $[C_6H_5CO_3H]/[C_6H_5CO_2H]$ determined in the reaction mixture after absorption of 20% of the amount of oxygen corresponding to the consumption required theoretically to oxidize benzaldehyde to peroxobenzoic acid. A parallel study of peroxobenzoic acid decomposition indicated that the different compositions of the reaction products found when using different catalysts were due to different effects of the catalysts on reactions (A) and (C).

It was of interest to establish what effect the oxidation state of metal had on the catalytic activity of the metal compound. Table II gives a comparison of the catalytic activities for the pairs Co(III)–Co(II) and Fe(III)–Fe(II). The data clearly show that the catalytic activities of the metals in their lower oxidation states are higher than the catalytic activities of the higher oxidation states. This conclusion finds support also in the fact that on exposure to light Fe(III), which is reduced by the effect of light to Fe(II), becomes an active catalyst of the reaction.

We examined how the course of the catalyzed oxidation of benzaldehyde is affected by additions of complexing compounds. Fig. 1 demonstrates the effect of ad-

TABLE I

Effects of catalysts on the composition of reaction mixture at 20% conversion of benzaldehyde ($c = 0.5 \text{ mol dm}^{-3}$) in benzene; 298 K; $[\text{O}_2] = \text{saturated}$

Catalyst $1 \cdot 10^{-5} \text{ mol dm}^{-3}$	Peroxybenzoic acid mol dm^{-3}	Benzoic acid mol dm^{-3}	Peroxybenzoic
			Benzoic
Mn(III) ethylcaproate	0.141	0.086	1.56
Fe(III) ethylcaproate	0.111	0.021	5.28
	0.116	0.027	4.30
	0.120	0.021	5.71
Ni(II) acetylacetonate	0.092	0.059	1.56
Cr(III) acetylacetonate	0.110	0.030	3.66
	0.115	0.029	3.96
Fe(III) acetylacetonate	0.117	0.010	11.7
	0.124	0.008	15.5
Co(II) acetylacetonate	0.133	0.020	6.65
	0.127	0.025	5.08
	0.125	0.021	5.95
	0.118	0.026	4.54
Co(III) acetylacetonate	0.110	0.039	2.82
	0.122	0.042	2.90
	0.117	0.043	2.72
	0.115	0.045	2.55

ditions of acetylacetonate on the reaction catalyzed by iron(III) acetylacetonate. It is clearly seen that the oxidation of benzaldehyde is inhibited by acetylacetonate. The inhibiting effects were also observed when using several other catalyzing complexes and adding complexing agents of different types.

It has been reported¹⁷ that peroxocompounds have catalytic effects on the oxidation of benzaldehyde. We have investigated the effects of dibenzoylperoxide and peroxobenzoic acid on the course of the oxidation, both in the absence and with additions of catalysts. However, none of these experiments showed evidence for catalytic effects of the peroxocompounds. It is likely that the observed catalytic effects of peroxocompounds on the so-called non-catalyzed reaction were, in fact, due to contamination of the reaction system by traces of transition metals.

Reaction Steps of the Catalyzed Oxidation of Benzaldehyde

The observation that metals in their lower oxidation states are more active catalysts for the oxidation of benzaldehyde than metals in the higher oxidation states cannot be explained in terms of the generally accepted concept of the reaction mechanism

TABLE II

Effect of the metal oxidation state on the rate of benzaldehyde oxidation. 10 ml of benzene solution of benzaldehyde ($c = 0.5 \text{ mol dm}^{-3}$); $[\text{O}_2] = \text{saturated}$; 298 K; RVL-X-250 arc; additions: 1 ml benzene solution of $[\text{Co}(\text{acac})_3]$ or $[\text{Co}(\text{acac})_2]$ ($c = 1 \cdot 10^{-4} \text{ mol dm}^{-3}$); 1 ml aqueous solution of FeCl_3 or FeSO_4 ($c = 1 \text{ mol dm}^{-3}$); 1 ml water or aqueous solution of FeCl_3 ($c = 1 \text{ mol dm}^{-3}$)

Time s	Oxygen consumption, ml					
	$[\text{Co}(\text{acac})_3]$	$[\text{Co}(\text{acac})_2]$	FeCl_3	FeSO_4	$h\nu$	$\text{FeCl}_3 + h\nu$
0	0	0	0	0	0	0
300	5.55	11.0	0.1	4.0	6.05	7.50
600	10.0	17.20	0.1	7.0	13.20	28.20
900	12.50	21.55	0.2	8.7	18.90	
1 200	15.05	24.20	0.2	9.8	23.0	
1 500	18.10		0.2	10.1		
1 800	19.30		0.3	10.4		
2 100	21.20		0.3	10.7		
2 400	22.50		0.3	10.9		
2 700	24.20		0.4	11.6		

(reactions (D)–(J)). It is particularly difficult to reconcile this observation with the concept of the initiation step represented by reaction (D).

The above observation together with results of a study on the photoinitiated reaction led us to the conclusion that the first step in the reaction catalyzed by metals in their higher oxidation states is apparently the reduction of the metals, resulting in the generation of catalytically active metal complexes. To verify this concept, we studied the reduction of metal complexes by benzaldehyde in an atmosphere of nitrogen, and the re-oxidation of the resulting lower oxidation states by dioxygen. In the discussion to follow, we consider only the results of the study on the reduction of iron(III) acetylacetonates. The results for acetylacetonates of other metals are difficult to interpret unambiguously. The absorption spectra show the formation of mixed-ligand complexes, and each system $[M(\text{acac})_3]$ –benzaldehyde will require a separate study.

Absorption spectrum of iron(III) acetylacetonate (Fig. 2) shows two maxima, at 439 nm and 355 nm. An addition of benzaldehyde produces an instantaneous decrease in the maximum at 439 nm which continues decreasing with time. The maximum at 355 nm grows as benzaldehyde is added, shifting at the same time to lo-

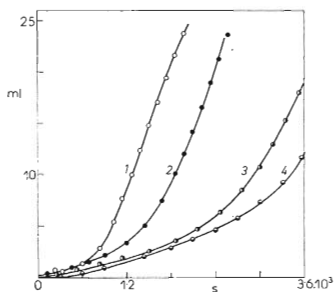


FIG. 1

Effect of acetylacetonate on the rate of benzaldehyde oxidation catalyzed by $[\text{Fe}(\text{acac})_3]$. 10 ml of benzene solution of benzaldehyde ($c = 0.5 \text{ mol dm}^{-3}$); $[\text{Fe}(\text{acac})_3]$ ($c = 5 \cdot 10^{-6} \text{ mol dm}^{-3}$); $[\text{O}_2] = \text{saturated}$; $T = 298 \text{ K}$; [acetylacetonate] (mol dm^{-3}): 1 0; 2 $1 \cdot 10^{-3}$; 3 $3 \cdot 10^{-3}$; 4 $6 \cdot 10^{-3}$

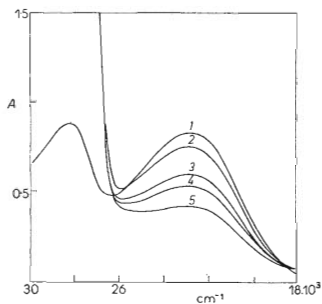


FIG. 2

Changes in the absorption spectrum of $[\text{Fe}(\text{acac})_3]$ on addition of benzaldehyde under N_2 . $[\text{Fe}(\text{acac})_3]$ in benzene ($c = 5 \cdot 10^{-4} \text{ mol dm}^{-3}$); N_2 ; $T = 298 \text{ K}$; benzaldehyde addition ($c = 4 \cdot 10^{-1} \text{ mol dm}^{-3}$) 1 no benzaldehyde; 2–5 at 0, 180, 360 and 10 800 s after addition

wer wavelengths. The decrease in the absorption maximum of iron(III) acetylacetonate is due to replacement of acetylacetonate in the coordination sphere by benzaldehyde, and to the reduction of iron(III) ion. That acetylacetonate is replaced by benzaldehyde is suggested by the fact that an addition of acetylacetonate gives rise to a marked increase in the absorbance at 439 nm. The reduction of the central Fe(III) ion to Fe(II) has been proved by reaction with *o*-phenanthroline.

In a further series of experiments we tested whether an addition of acetylacetonate would have an effect on the rate of the reduction of iron(III) acetylacetonate by benzaldehyde. The results presented in Fig. 3 show that similarly to the inhibition in the oxidation of benzaldehyde by dioxygen (Fig. 1), acetylacetonate inhibits also the reduction of iron(III) acetylacetonate, *i.e.* the reaction step which we suppose to be involved in the catalyzed oxidation of benzaldehyde by dioxygen.

If the reduction of iron(III) acetylacetonate proceeds at a slight excess of acetylacetonate (about ten-fold; a larger excess, say, a hundred-fold one, will completely suppress the reduction), a substance is formed which gives an absorption maximum at 650 nm. This maximum disappears on bubbling the solution with oxygen. At the same time, the initial maximum at 436 nm corresponding to iron(III) acetylacetonate reappears, and is restored to the initial height if acetylacetonate is added. The absorption maximum at 650 nm reappears after the oxygen supply has been shut off. This reduction-oxidation cycle can be repeated several times (Fig. 4). It is difficult to decide what is the occupation of the coordination sphere of Fe(II) in the coloured complex (λ_{\max} 650 nm); yet in view of the composition of the reaction solution we believe that the characteristic spectrum is due either to the complex $[\text{Fe(II)(acac)}_2]$ or to the mixed-ligand complex $[\text{Fe(II)(acac)(benzaldehyde)}]$.

REACTION MECHANISM

"Non-Catalyzed" Reaction

A characteristic feature of the oxidation of benzaldehyde is remarkable dependence of its course on trace impurities. This observation is easy to understand if we consider the nature of the reaction between benzaldehyde and dioxygen.

The reaction between benzaldehyde and dioxygen is one between a singlet molecule and a triplet molecule to yield a singlet molecule. According to the spin conservation principle this reaction is "spin-forbidden", and requires a high activation energy. In the presence of transition metal ions, complexes with dioxygen or mixed-ligand complexes with benzaldehyde and dioxygen are generated whose reactions are not forbidden on spin grounds. This fact can explain the experimental observation that transition metal ions catalyze the reaction of benzaldehyde with dioxygen, and that they do so even when present in trace concentrations. Since it is impossible to prepare absolutely pure systems, it is equally impossible to eliminate completely

the influence of trace impurities which are responsible for seemingly inexplicable effects.

Catalyzed Reaction

The concept of the mechanism of the catalyzed reaction is based on the results of studies on the course of the reaction catalyzed by various metal complexes, and on the more detailed study of the reaction catalyzed by iron(III) acetylacetonate.

The study on the course of the reaction catalyzed by various complexes revealed that the catalytic activity of transition metals is higher when they assume their lower oxidation states.

The investigation of the reaction catalyzed by iron(III) acetylacetonate has established that the catalyzed reaction involves reduction of Fe(III) to Fe(II), the latter having been proved to be the catalyst of the reaction, and re-oxidation of Fe(II) to Fe(III). It is uncertain whether Fe(III) has any catalytic effect on the oxidation of benzaldehyde by dioxygen.

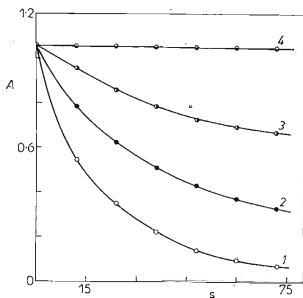


FIG. 3

Effect of acetylacetonate on the rate of reaction between $[\text{Fe}(\text{acac})_3]$ and benzaldehyde. 1 mol benzaldehyde + $1.6 \cdot 10^{-4}$ mol $[\text{Fe}(\text{acac})_3]$ in 1 dm³ benzene; $T = 298$ K; acetylacetonate additions (mol dm⁻³): 1 0; 2 $1 \cdot 10^{-3}$; 3 $2 \cdot 10^{-3}$; 4 $3 \cdot 10^{-3}$.

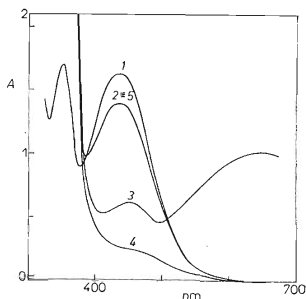


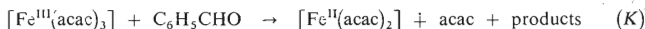
FIG. 4

Absorption spectra of the systems $[\text{Fe}(\text{acac})_3]$ + acac + benzaldehyde + N₂, $[\text{Fe}(\text{acac})_3]$ + acac + benzaldehyde + O₂. $4 \cdot 10^{-4}$ mol $[\text{Fe}(\text{acac})_3]$ + $5 \cdot 10^{-3}$ mol acac in 1 dm³ benzene; $T = 298$ K; 1 no benzaldehyde, N₂; 2 immediately after addition of benzaldehyde ($c = 1$ mol dm⁻³), N₂; 3 solution 2 after 3 600 s, N₂; 4 solution 3 bubbled with oxygen (5 s); 5 $5 \cdot 10^{-3}$ mol dm⁻³ acac added to solution 4

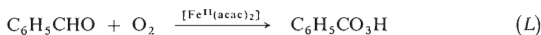
A mechanism for the reaction catalyzed by iron(III) acetylacetonate compatible with these findings involves as the first step the reduction of iron(III) acetylacetonate by benzaldehyde to give iron(II) acetylacetonate (equation (K)) which catalyzes the oxidation of benzaldehyde by dioxygen (equation (L)). Simultaneously with the catalyzed oxidation of benzaldehyde, there occurs re-oxidation of iron(II) acetylacetonate (equation (M)) which represents deactivation of the catalyst.

Mechanism of Catalyzed Reaction

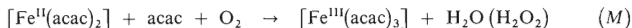
Catalyst generation:



Catalyzed reaction:



Catalyst deactivation:



The proposed mechanism accounts for the experimental observations made in the study of the reaction catalyzed by iron(III) acetylacetonate, and is also in accord with the observed features of the photoinitiated reaction (*c.f.*, ref.¹⁹). It is justifiable to believe that essentially the same mechanism would hold for the autoxidation of benzaldehyde catalyzed by other metal complexes. It is not possible, for the time being, to draw up a more detailed mechanism of the reaction. Each of the reaction steps considered has its own mechanism which depends on the nature of both the metal and the bonded ligands. Reactions of these types in non-aqueous media have received, to our knowledge, very little study.

With its three isolated steps (equations (K)–(M)), the proposed mechanism resembles, on the formal side, the free radical chain mechanism. However, the comparison cannot be carried any further, since the reaction steps involved are of essentially different nature.

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