OXIDATION OF 1,2,3,4-TETRAHYDRONAPHTHALENE BY DIOXYGEN. EFFECTS OF 3d TRANSITION METAL 2,4-PENTANEDIONATES ON THE THERMAL AND PHOTOINITIATED REACTIONS

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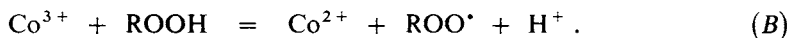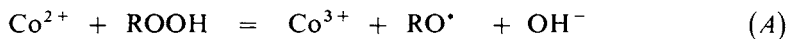*Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 160 00 Prague 6*

The effects of Mn^{III}, Co^{II}, Co^{III}, Fe^{III}, and Cr^{III} 2,4-pentanedionates on the thermal and photo-initiated oxidation reactions of 1,2,3,4-tetrahydronaphthalene by dioxygen have been investigated. Co^{II} and Mn^{III}, which are highly efficient catalysts for the thermal reaction, do not increase the rate of the photoinitiated reaction. Fe^{III} and Co^{III}, which are poorly active in catalyzing the thermal reaction, have profound photocatalytic effects. The catalytic effect of Cr^{III} is critically dependent on the presence of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide. An increase in the reaction temperature increases the rate of the photoinitiated reaction and enhances the catalytic and photocatalytic effects.
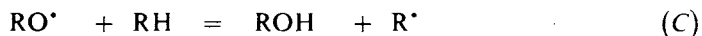
The thermal and photoinitiated oxidation reactions of 1,2,3,4-tetrahydronaphthalene (tetralin) have been used over a period of years as model reactions in studies of the oxidation of hydrocarbons by dioxygen[1-9]. Although the effect of transition metal compounds on these reactions has long been known, the mechanism of their action is not yet understood. It is often assumed that transition metal compounds catalyze the oxidation of hydrocarbons by reacting with hydroperoxide, the primary product of the oxidation, to form free radicals which initiate the propagation cycle of the oxidation.
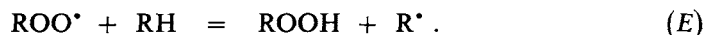
A typical example of classical free radical chain mechanism is the reaction scheme, $(A)-(F)$, proposed by Kamiya and coworkers[6] for the oxidation of tetralin by dioxygen catalyzed by cobalt(II) acetate (RH = tetralin; ROOH = 1,2,3,4-tetra-hydro-1-naphthyl hydroperoxide (α-tetralin hydroperoxide); ROH = 1,2,3,4-tetra-hydro-1-naphthol (α-tetralol)):
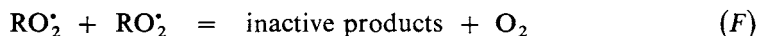
Initiation reactions:

$$Co^{2+} + ROOH = Co^{3+} + RO^{\bullet} + OH^{-} \tag{A}$$

$$Co^{3+} + ROOH = Co^{2+} + ROO^{\bullet} + H^{+}. \tag{B}$$

Propagation reactions:

$$RO^{\bullet} + RH = ROH + R^{\bullet} \tag{C}$$

$$R^{\bullet} \quad + O_2 \quad = \quad ROO^{\bullet} \tag{D}$$

$$ROO^{\bullet} + RH \quad = \quad ROOH + R^{\bullet} . \tag{E}$$

Termination reactions:

$$RO_2^{\bullet} + RO_2^{\bullet} \quad = \quad \text{inactive products} + O_2 \tag{F}$$

other free radical reactions giving non-radical products.

According to this classical concept, the catalyst affects only the initiation reaction, *i.e.* the generation of free radicals which start the propagation cycle. Later studies[7,10] consider the participation of the catalyst also in the terminating reactions. Our aim in the present work was to contribute to the elucidation of the mechanism by which $3d$ transition metal 2,4-pentanedionates catalyze the thermal and photoinitiated oxidation reactions of tetralin by dioxygen.

EXPERIMENTAL

Chemicals

Special care was taken to ensure high purity of tetralin. A commercial product was first freed of the major part of peroxidic compounds by shaking with a saturated sulphite solution in an atmosphere of nitrogen over a period of several days. So treated tetralin was dried by anhydrous sodium sulphate, vacuum distilled, and finally vacuum rectified. The middle fraction was retained. The content of peroxidic compounds in 1 dm^3 of tetralin purified in this way was lower than 10^{-4} mol. The tetralin was stored in sealed ampoules under nitrogen in the absence of light.

The following 2,4-pentanedionates (acetylacetonates = acac) were used as catalysts: [Fe(acac)$_3$], [Co(acac)$_2$], [Co(acac)$_3$], [Mn(acac)$_3$], and [Cr(acac)$_3$]. All the 2,4-pentanedionates except [Fe(acac)$_3$] (Merck, Darmstadt) were prepared according to published procedures[11]. Solid [Co(acac)$_2$] was stored in a desiccator over silicagel to prevent its strong tendency to bind water and hydrolyze. Benzene solutions of [Co(acac)$_2$] also showed a tendency to hydrolyze, presumably due to the presence of small amounts of water, and were therefore prepared immediately before starting each experiment. There was some tendency for [Mn(acac)$_3$] to precipitate from the solution. The other 2,4-pentanedionates formed stable benzene solutions.

Experimental Arrangement and Procedure

The oxidation of tetralin (10 ml of 5 mol dm^{-3} solution in n-heptane) was carried out in a thermostatted quartz vessel connected to a gas burette filled with oxygen. The course of the reaction was followed by measuring the amount of consumed oxygen. In most experiments, the measurements were only made during the initial stages of the reaction up to an overall oxygen consumption of 50 ml, *i.e.* no more than 5% of the theoretical amount of oxygen required for complete conversion of tetralin to tetralin hydroperoxide.

The procedure was as follows. The reaction vessel was charged with 10 ml of 5 mol dm^{-3} solution of tetralin in n-heptane, and 0·1 ml of a benzene solution of catalyst was added. Comparative experiments established that the amount of benzene added had no measurable effect on

the rate of tetralin oxidation. The reaction system was closed and allowed to equilibrate for 15 min. The measurement of oxygen consumption was started 1 min after switching on the shaking, a time long enough for saturation of the reaction solution with oxygen and short enough compared to the overall reaction period.

The photochemical reaction was initiated by the full output of an HBO 500 W high-pressure mercury lamp (Narva, Berlin). The lamp was placed in an aluminium block which ensured a constant moderate cooling and hence a constant light flux. In order to achieve a better utilization of the light flux, the HBO 500 W lamp was placed at the focus of a condensing lens.

Fig. 1 shows absorption spectra of tetralin solutions in n-heptane ($1 . 10^{-3} - 5$ mol dm^{-3}) as well as the main emission lines of the HBO 500 W lamp used. By comparing the emission spectrum of the lamp with the absorption spectrum of 5 mol dm^{-3} tetralin solution, it can be seen that the majority of the absorbed photons had wavelengths of 297 nm, 303 nm, and 313 nm. As seen from Figs 2 and 3, the amounts of 2,4-pentanedionates added markedly increase light absorption at wavelengths greater than 320 nm, *i.e.* for the mercury lines 334 nm and 365 nm, and in the case of [Fe(acac)$_3$] also for the 436 nm line.

In order that the effects of added 2,4-pentanedionates on the thermal and photoinitiated oxidation reactions of tetralin be unambiguously distinguished, the thermal reaction was always followed for 30 min before starting the photochemical reaction. Moreover, in order to distinguish the direct effect of the ultraviolet radiation from the effects of the substances generated in the photoinitiated reaction (photochemically generated catalyst and tetralin hydroperoxide produced by the oxidation), the thermal reaction was also followed for a minimum of 30 min after termination of irradiation.
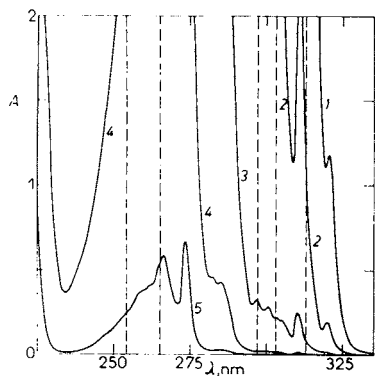

Fɪɢ. 1

Absorption spectra of tetralin solutions in n-heptane. 1 cm cell; 20°C; [tetralin]: *1* 5 mol dm^{-3}; *2* 1 mol dm^{-3}; *3* 0·1 mol . . dm^{-3}; *4* 1 . 10^{-2} mol dm^{-3}; *5* 1 . . 10^{-3} mol dm^{-3}. Dashed line: main emission lines of the HBO 500 W high-pressure mercury lamp used

Fɪɢ. 2

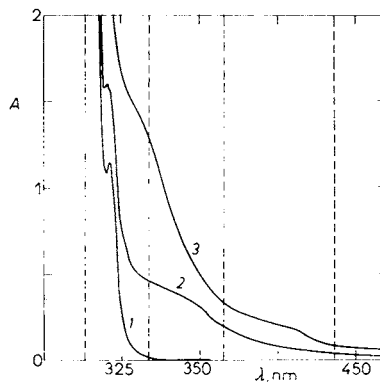Absorption spectra of 5 mol dm^{-3} solution of tetralin in n-heptane with added [M(acac)$_n$] ($1 . 10^{-4}$ mol dm^{-3}). 1 cm cell; 20°C; *1* no [M(acac)$_n$] added; *2* [Co(acac)$_2$]; *3* [Mn(acac)$_3$]. Dashed line: main emission lines of HBO 500 W lamp

RESULTS AND DISCUSSION

Effects of $[M(acac)_n]$ on the Thermal and Photoinitiated Reactions

The first step in our study was to compare the catalytic effects of Co^{II}, Co^{III}, Mn^{III}, Fe^{III}, and Cr^{III} 2,4-pentanedionates on the thermal and photoinitiated reactions. According to their catalytic and photocatalytic effects, the 2,4-pentanedionates can be divided into three groups:

I. The first group comprises $[Co(acac)_2]$ and $[Mn(acac)_3]$ (see Fig. 4). These compounds are highly active catalysts for the thermal reaction, their catalytic effects being noticeable at room temperature even at relatively low concentrations. During the course of the oxidation, both compounds lose their catalytic activity, so that the oxidation rate decreases with increasing conversion. They do not increase the rate of the photoinitiated reaction.

II. The second group (see Fig. 5) comprises $[Co(acac)_3]$ and $[Fe(acac)_3]$. Compared with the first group, these substances are considerably poorer catalysts for the thermal reaction; even when added to concentrations of the order of 10^{-4} mol dm^{-3}, they produce catalytic effects only upon elevating the temperature to about 60°C. During the course of the oxidation, their catalytic effects tend to increase slightly
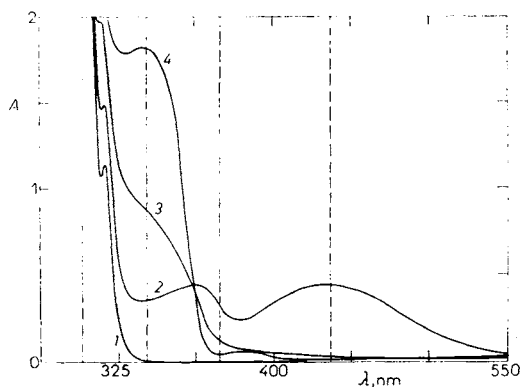
FIG. 3

Absorption spectra of 5 mol dm^{-3} solution of tetralin in n-heptane with added [M(acac)$_n$] (1 . 10^{-4} mol dm^{-3}). 1 cm cell; 20°C; *1* no [M(acac)$_n$] added; *2* [Fe(acac)$_3$]; *3* [Co(acac)$_3$]; *4* [Cr(acac)$_3$]. Dashed line: main emission lines of HBO 500 W lamp
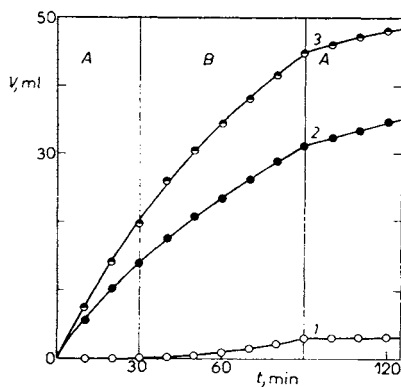
FIG. 4

Thermal (*A*) and photoinitiated (*B*) oxidations of tetralin by dioxygen. $V =$ ml O$_2$; 5 mol dm^{-3} solution of tetralin in n-heptane; 60°C; photochemical reaction initiated by the full output of a HBO 500 W lamp; *1* no [M(acac)$_n$] added; *2* 1 . 10^{-4} mol . dm^{-3} [Mn(acac)$_3$]; *3* 1 . 10^{-4} mol dm^{-3} [Co(acac)$_2$]

and consequently the oxidation catalyzed by these substance shows a slightly auto-catalytic character. Both catalysts markedly increase the rate of the photoinitiated oxidation of tetralin by dioxygen. The interpretation of the photocatalytic effect of $[Co(acac)_3]$ is straightforward: radiation causes a reduction of the catalytically poorly active $[Co(acac)_3]$ to $[Co(acac)_2]$ with a substantially higher catalytic acti-vity. The mechanism of the photocatalytic effect of $[Fe(acac)_3]$ may be expected to be analogous.

III. The third type of catalyst (see Fig. 6) is represented by $[Cr(acac)_3]$. Its cata-lytic effect is critically dependent on the presence of tetralin hydroperoxide and increases sharply with increasing concentration of tetralin hydroperoxide. The oxidation of tetralin by dioxygen catalyzed by $[Cr(acac)_3]$ therefore exhibits distinct autocatalytic features. In the early stages the rate of the photoinitiated oxidation in the presence of $[Cr(acac)_3]$ is higher than with no catalyst added. This difference is due to the effect the photochemically generated tetralin hydroperoxide has on the catalytic activity of $[Cr(acac)_3]$. In later stages when the photochemically generated tetralin hydroperoxide constitutes only a small fraction of the total concentration of tetralin hydroperoxide, irradiation has no longer an effect on the rate of tetraline oxidation in the presence of $[Cr(acac)_3]$. This assertion is illustrated in Fig. 6 by the kinetics after termination of irradiation.
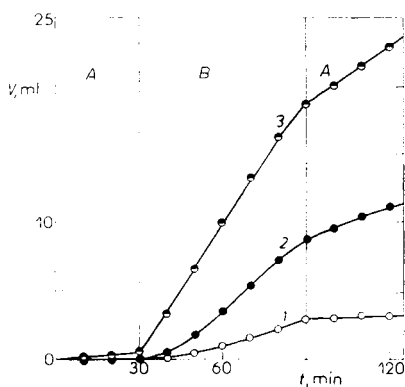

FIG. 5

Thermal (*A*) and photoinitiated (*B*) oxida-tions of tetralin by dioxygen. $V = ml\ O_2$; 5 mol dm^{-3} solution of tetralin in n-hep-tane; 60°C; photochemical reaction initiated by the full output of a HBO 500 W lamp; *1* no [M(acac)$_n$] added; *2* 1 . 10^{-4} mol dm^{-3} [Fe(acac)$_3$]; *3* 1 . 10^{-4} mol dm^{-3} [Co(acac)$_3$]
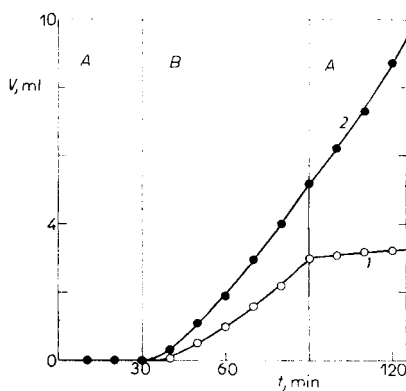
FIG. 6

Thermal (*A*) and photoinitiated (*B*) oxida-tions of tetralin by dioxygen. $V = ml\ O_2$; 5 mol dm^{-3} solution of tetralin in n-hep-tane; 60°C; photochemical reaction initiated by the full output of a HBO 500 W lamp; *1* no [M(acac)$_n$] added; *2* 1 . 10^{-4} mol . dm^{-3} [Cr(acac)$_3$]

The rate of tetralin oxidation by dioxygen may be affected even by trace concentrations of a catalyst. This is illustrated in Fig. 7, which shows kinetic curves for the oxidation at various concentrations of added $[Co(acac)_2]$. It can be seen that, under the experimental conditions used, there is a measurable increase in the oxidation rate on adding $[Co(acac)_2]$ to concentrations as low as $1 . 10^{-7}$ mol dm^{-3}. This indicates that in measurements of reaction rates with no added catalyst the results are affected by the catalytic activity of transition metals present in the reaction system as trace impurities.

By comparing Figs 8 and 9 it can be seen that there is a difference between the rates of reactions started by $[Co(acac)_2]$ and $[Co(acac)_3]$ over the whole range investigated. This observation is important for considerations of the mechanism of initiation, for it signifies that the hypothetical reactions (A) and (B) do not proceed so rapidly as to cause the decomposition of tetralin hydroperoxide with repeated (A)–(B) cycles. The catalyst concentrations used were $1 . 10^{-4}$ mol dm^{-3} and lower. A comparable concentration of tetralin hydroperoxide is produced on consumption of 0·02 ml of oxygen. Thus, there is a large excess of tetralin hydroperoxide relative to the catalyst concentration over the whole conversion range examined here.

$[Co(acac)_2]$ and $[Mn(acac)_3]$, which exhibit a high catalytic activity in the thermal reaction, lose their activity in the course of the oxidation. These compounds can be considered to be the catalytically active species. $[Co(acac)_3]$, $[Fe(acac)_3]$, and $[Cr(acac)_3]$, on the other hand, show by themselves very low catalytic activities and gain (or increase) their catalytic effects by the action of tetralin hydroperoxide[12] (this is the case chiefly with $[Cr(acac)_3]$ and to a lesser extent with $[Co(acac)_3]$ and $[Fe(acac)_3]$) or on exposure to UV radiation ($[Co(acac)_3]$ and $[Fe(acac)_3]$). Thus they may be considered as catalyst precursors. In accord with this concept is also the following experimental observation: the catalysts that have marked effects on the thermal reaction ($[Co(acac)_2]$ and $[Mn(acac)_3]$) do not accelerate the photo-initiated reaction and conversely, the catalysts that exhibit photocatalytic effects ($[Co(acac)_3]$ and $[Fe(acac)_3]$) show only very low activities for the thermal reaction.

Effect of Temperature on the Thermal and Photoinitiated Reactions

Up to the present time, no attention has been paid to the effect of temperature on the photoinitiated oxidation of tetralin by dioxygen. This also applies more generally to photoinitiated oxidation reactions of organic compounds with oxygen (we know of only one study[13] in which the effect of temperature is mentioned). The lack of interest in studying the effect of temperature on photoinitiated reactions has its roots in the accepted mechanistic concepts, according to which the propagation reactions (C), (D), and (E) have very low activation energies and hence are very weakly dependent on temperature.

In conflict with these concepts, we have found that the reaction temperature determines the rate of tetralin oxidation by dioxygen even in the photoinitiated

reaction. Fig. 9 shows kinetic curves for the photoinitiated oxidation of tetralin by dioxygen at temperatures in the range $20-80°C$. The observed dependence
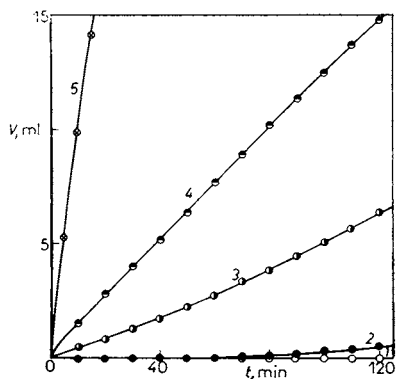

FIG. 7

Effect of [Co(acac)$_2$] concentration on the thermal oxidation of tetralin by dioxygen. V = ml O$_2$; 5 mol dm^{-3} solution of tetralin in n-heptane; 70°C; *1* no [Co(acac)$_2$] added; [Co(acac)$_2$]; *2* 1 . 10^{-7} mol dm^{-3}; *3* 1 . . 10^{-6} mol dm^{-3}; *4* 1 . 10^{-5} mol dm^{-3}; *5* 1 . 10^{-4} mol dm^{-3}
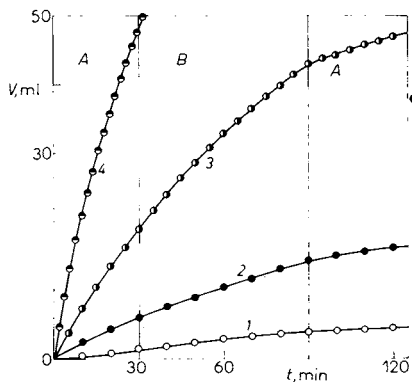
FIG. 8

Effect of temperature on thermal (*A*) and photoinitiated (*B*) oxidations of tetralin by dioxygen ($V=$ ml O$_2$) catalyzed by 1 . . 10^{-4} mol dm^{-3} [Co(acac)$_2$]. 5 mol dm^{-3} solution of tetralin in n-heptane; photochemical reaction initiated by the full output of a HBO 500 W lamp; *1* 20°C; *2* 40°C; *3* 60°C; *4* 80°C
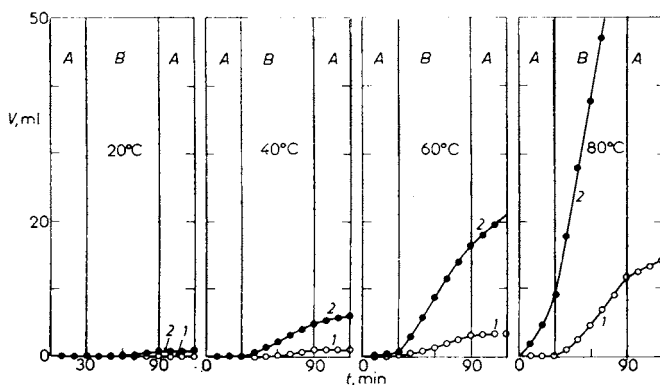

FIG. 9

Effect of temperature on thermal (*A*) and photoinitiated (*B*) oxidations of tetralin by dioxygen ($V =$ ml O$_2$). 5 mol dm^{-3} solution of tetralin in n-heptane; photochemical reaction initiated by the full output of a HBO 500 W lamp; *1* no catalyst added; *2* 1 . 10^{-4} mol dm^{-3} [Co(acac)$_3$]

indicates that the rate-determining step of the photoinitiated reaction is temperature dependent, which implies that the rate is controlled by some of the secondary thermal reactions.

An increase in temperature increases not only the catalytic but also the photocatalytic effects. The enhancement of the photocatalytic effects in tetralin oxidation by dioxygen catalyzed by $[Fe(acac)_3]$ has been described in our previous paper[14]. As documented in Fig. 9, an increase in temperature increases the photocatalytic effects also in the reaction catalyzed by $[Co(acac)_3]$. In a previous discussion of this phenomenon we have shown that even subanalytical concentrations of transition metals may become catalytically effective upon increasing the temperature[15]. Accordingly, it is not ruled out that the increase in the rate of oxidation with no catalyst added is due to enhancement of the catalytic activity of transition metals present in the reaction system as trace impurities.

Fig. 10 demonstrates the validity of the Arrhenius equation $(\ln k \ vs \ 1/T)$ for the photoinitiated oxidation of tetralin with no added catalyst. Since the kinetics of tetralin oxidation does not follow a simple rate law, the rate constants were replaced by average rates of tetralin oxidation, $\bar{v}$, expressed as millilitres of oxygen consumed in 1 s. It may be seen from Fig. 10 that the values of $\bar{v}$ give a reasonably good fit to the linearized Arrhenius equation over the temperature range investigated (40 to 80°C) irrespective of whether the $\bar{v}$ is calculated from the oxygen consumption at 10 min, 30 min or 60 min, *i.e.* irrespective of the degree of conversion. The apparent activation energy is found to be 55 kJ mol^{-1}, a value unexpectedly high for a propagation step.

Within the framework of classical free radical chain mechanism, one other consequence of an increase in the rate of a photoinitiated reaction on increasing the reaction temperature is that the kinetic chain length must also increase, and it must do so in direct proportion to the increase in the rate. (The kinetic chain length is
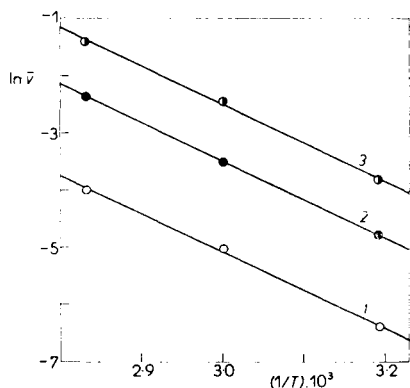

FIG. 10

Arrhenius plot $(\ln \bar{v} \ vs \ 1/T)$ for the photoinitiated oxidation of 5 mol dm^{-3} tetralin in n-heptane. Initiated by the full output of a HBO 500 W lamp; $\bar{v}$ (ml O$_2$/s) — average reaction rate after *1* 10 min; *2* 30 min; *3* 60 min reaction

usually defined[16] as the number of propagation cycles that occur before the chain is interrupted.) In view of the assumed low activation energies of the propagation steps, it is surprising that the kinetic chain length should increase.

CONCLUSION

The oxidation of tetralin by dioxygen is a trace catalyzed reaction; mechanistic conclusions must be derived from a study of the catalyzed reaction.

The difference found between the rates of tetralin oxidation catalyzed by $[Co(acac)_2]$ and $[Co(acac)_3]$ indicates that the oxidation is not initiated by the $Co^{II}-Co^{III}$ cycle, as is often assumed in oxidation reactions.

As a consequence of the adherence to unsound mechanistic concepts, the reaction temperature has as yet been completely disregarded as a factor in photoinitiated oxidation reactions of singlet substrates with oxygen. However, the observed apparent activation energy of 55 kJ mol^{-1} indicates that the rate of the photoinitiated oxidation of tetralin is profoundly affected by the reaction temperature.

The present study has revealed photocatalytic effects of Co^{III} and Fe^{III} 2,4-pentanedionates, which probably consist in photochemical generation of catalytically more active, lower oxidation states.

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Translated by M. Škubalová.