

Oxidation of Tetraline by Dioxygen. Effect of $\text{Fe}(\text{acac})_3$ on the Thermal and Photoinitiated Reactions

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The photochemical oxidation of tetraline by dioxygen is catalyzed by ferric acetylacetonate (iron(III) 2,4-pentadionate), the reaction rate increasing markedly with temperature. The rate-determining step of the photochemical oxidation is presumably a catalyzed thermal reaction.

The reaction of dioxygen with tetraline, like reactions of other singlet substrates, is spin-forbidden, and accordingly it proceeds very slowly at room temperature. The reaction rate can be increased substantially [1–6] either by raising the temperature of the reaction mixture containing an addition of a catalytically active transition metal compound or by exposure to ultraviolet radiation.

We have found recently [7–9] that transition metal compounds play a decisive role also in the photochemical oxidation of some singlet substrates. The aim of the present work was to examine the effect of $\text{Fe}(\text{acac})_3$ on the photoinitiated oxidation of tetraline by dioxygen at various temperatures.

The oxidation of tetraline (5 M-solution in *n*-heptane) was carried out in a thermostatted quartz vessel connected to a thermostatted gas burette filled with oxygen. The quartz vessel was vigorously shaken. The reaction course was followed volumetrically by measuring the consumption of oxygen. The tetraline was twice vacuum distilled, vacuum rectified, and stored in sealed ampoules filled with a protective atmosphere of nitrogen. The *n*-heptane was UV spectroscopy grade (Lachema).

The ultraviolet radiation for the study of the photoinitiated reaction was obtained from a HBO 500 W high-pressure mercury arc (Osram) housed in an aluminium cooling block ensuring a mild constant cooling and thereby a constant light flux. The radiation was not filtered in order for the highest possible light flux to be achieved. Comparison of the absorption spectrum of the 5 M-tetraline solution with the emission spectrum of the HBO 500 arc showed that the photochemical reaction

was initiated by light of 303 nm, 313 nm, 334 nm, and 365 nm.

In each experiment the reaction was allowed to proceed for 120 min. In order to achieve rigorous discrimination between the catalytic and photocatalytic effects, the thermal reaction in each run was followed for 30 min before starting the photoinitiated reaction. After irradiation the thermal reaction was again followed for 30 min so that the effect of the UV radiation could be discerned from the effect of the hydroperoxide formed on the thermal reaction.

In the first series of experiments we examined the effect of the reaction temperature on the rate of the thermal oxidation of tetraline without a catalyst and with an addition of 1×10^{-4} M ferric acetylacetonate ($\text{Fe}(\text{acac})_3$). In the absence of catalyst, the thermal reaction was found to proceed at an extremely slow rate throughout the studied temperature range 20–80 °C (Fig. 1). On addition of 1×10^{-4} M $\text{Fe}(\text{acac})_3$ the rate remained low in a temperature range from 20 to 60 °C. Increasing the temperature above 60 °C, however, resulted in a steep rise in the reaction rate. As documented in Fig. 1, the rate increase in the range 60–80 °C occurs to a marked extent only on addition of $\text{Fe}(\text{acac})_3$ to the reaction mixture.

The second series of experiments explored the effect of $\text{Fe}(\text{acac})_3$ addition on the rate of the photo-

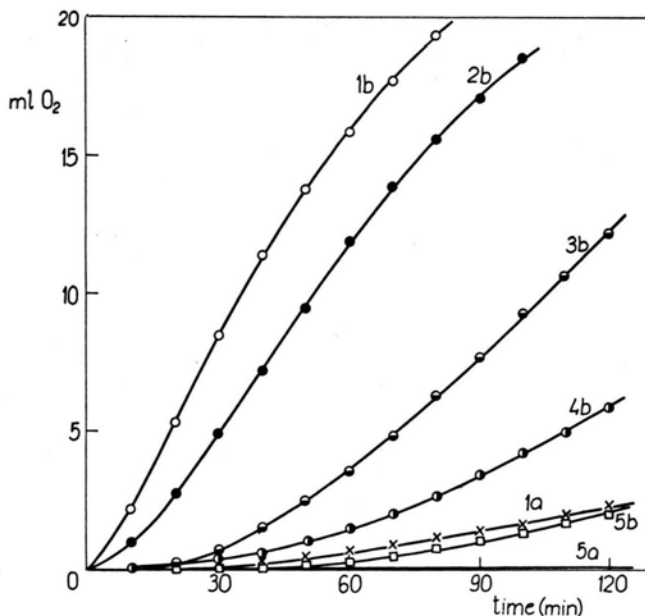


Fig. 1. Effect of temperature on the thermal oxidation of tetraline by dioxygen. $[\text{tetraline}]_0 = 5$ M in *n*-heptane; a) no catalyst added; b) an addition of 1×10^{-4} M $\text{Fe}(\text{acac})_3$; 1. — 80 °C; 2. — 75 °C; 3. — 70 °C; 4. — 65 °C; 5. — 60 °C.

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initiated reaction at various temperature. The results are presented in Fig. 2, in which it is seen that at temperatures between 20 and 60 °C the

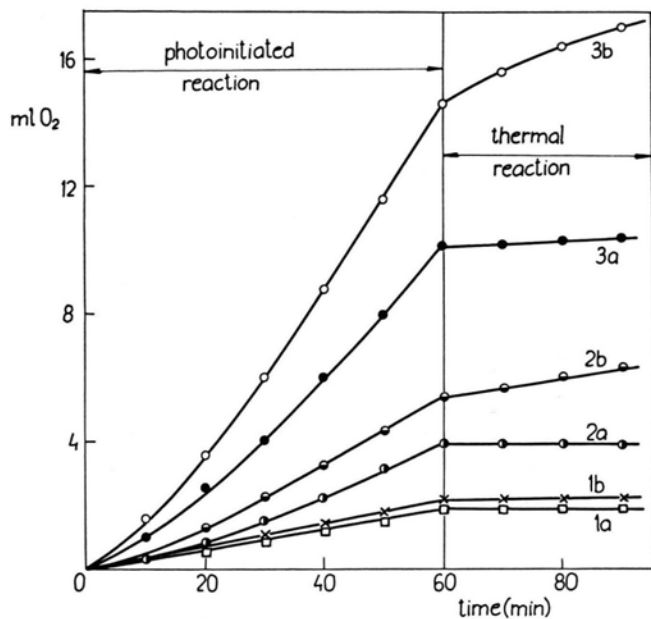


Fig. 2. Effect of temperature on the photoinitiated oxidation of tetraline by dioxygen. $[\text{tetraline}]_0 = 5 \text{ M}$ in *n*-heptane; initiated by the whole spectrum of a HBO 500 high-pressure mercury arc (Osram); a) no catalyst added; b) an addition of $1 \times 10^{-4} \text{ M Fe}(\text{acac})_3$; 1.—20 °C; 2.—40 °C; 3.—60 °C.

addition of $\text{Fe}(\text{acac})_3$ enhances the rate of the photoinitiated reaction and that this effect becomes more pronounced with increasing temperature. The apparent activation energy calculated from the temperature dependence of the rate of the photoinitiated reaction is 50 kJ/mol. That we are indeed dealing with temperature dependence of the photoinitiated reaction can be seen from comparison with the reaction kinetics observed after terminating the irradiation: if the increase in the overall reaction rate were due to the effect of the tetraline hydroperoxide that is formed, it would have to continue on termination of irradiation. The value found for the apparent activation energy is slightly beyond the interval of values usually considered [10] for free radical chain reactions.

The observation of the pronounced temperature dependence of the rate of the photoinitiated oxidation of tetraline by dioxygen is of relevance to consideration of the reaction mechanism, for it implies that the rate-determining step is some of the thermal reactions that occur following the absorption of a light quantum. As noted above, the value of the activation energy, 50 kJ/mol, appears to be rather high for a free radical and, in addition, a chain propagation reaction. The observed photocatalytic effects of transition metal compounds clearly indicate that transition metals play an important role even in the mechanism of the photochemical oxidation of tetraline by dioxygen. It seems justifiable to assume that the same mechanism as has been proved for some other spin-forbidden reaction of dioxygen [9, 11–13] is operative also in the photoinitiated oxidation of tetraline.

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