

**PHOTOCHEMICAL DECOMPOSITION OF t-BUTYL HYDROPEROXIDE;
PHOTOCATALYTIC EFFECTS OF VO(II) AND Co(III)
2,4-PENTANEDIONATES**

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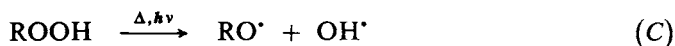
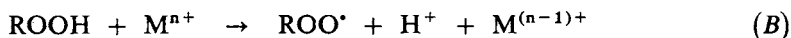
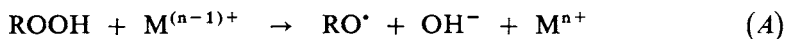
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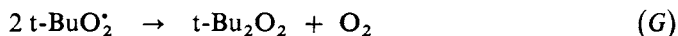
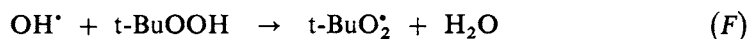
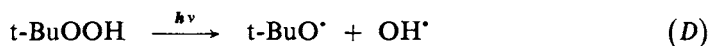
It has been found that [VO(acac)₂] and [Co(acac)₃] increase the rate of t-BuOOH photolysis, whereas [Fe(acac)₃] has the opposite effect. Redox changes of the catalytically active [VO(acac)₂] were followed using the EPR technique. An EPR signal from a free radical intermediate of photochemical decomposition of t-BuOOH was recorded, and the concentration of the intermediate was monitored during the reaction.

The decomposition of hydroperoxides plays an important role in the oxidation of organic compounds by dioxygen¹⁻³. According to classical concepts², the oxidation of organic compounds by dioxygen is initiated either by catalytic decomposition of hydroperoxide (reactions (A) and (B)) or by its thermal or photochemical dissociation (reaction (C)).



Recently, we have demonstrated⁴⁻⁶ that transition metal compounds can efficiently catalyze even photoinitiated oxidations. This raises the question of how these compounds influence the photolysis of organic hydroperoxides, the primary products in oxidations of organic compounds by dioxygen. The importance of resolving this question is underlined by the recently demonstrated effect of free radical initiators on the catalyst activity, namely that an increase in the concentration of a free radical initiator may lead to a decrease in the rate of catalyzed oxidation of an organic compound by dioxygen⁷.

It has been reported⁸⁻¹² that UV radiation breaks the O—O bond in t-BuOOH with the formation of alkoxy and hydroxy radicals. The most frequently considered reactions are as follows.



The aim of the present work was to investigate the effects of $[\text{VO}(\text{acac})_2]$, $[\text{Co}(\text{acac})_3]$, and $[\text{Fe}(\text{acac})_3]$ (acac stands for 2,4-pentanedionate), i.e. of compounds which catalyze photoinitiated oxidations of hydrocarbons by dioxygen, on the photolysis of $t\text{-BuOOH}$.

EXPERIMENTAL

Chemicals

The starting t -butyl hydroperoxide was prepared by oxidation of t -butyl alcohol by 30% hydrogen peroxide in sulphuric acid medium¹³. $[\text{Co}(\text{acac})_3]$ and $[\text{VO}(\text{acac})_2]$ were prepared as described in the literature¹⁴, and $[\text{Fe}(\text{acac})_3]$ was obtained from Merck (Darmstadt). Analytical grade toluene and benzene (Lachema) were used as supplied.

Procedure and Methods

The photolysis of $t\text{-BuOOH}$ was run in a thermostatted quartz vessel provided with a septum for sampling without disturbing a protective atmosphere of nitrogen. The photochemical reaction was initiated by the whole spectrum of an HBO 500 W high-pressure mercury arc (Narva, Berlin). In most cases, the reaction was carried out with 30 ml of solution containing 0.1 mol dm^{-3} $t\text{-BuOOH}$ and $1 \cdot 10^{-3} \text{ mol dm}^{-3}$ $[\text{VO}(\text{acac})_2]$, $[\text{Co}(\text{acac})_3]$ or $[\text{Fe}(\text{acac})_3]$. The solution was stirred by a magnetic stirrer and was thermostatted at 298 K. The concentration of $t\text{-BuOOH}$ was determined at regular time intervals by iodometric titration of samples of the reaction solution¹⁵.

EPR spectra were taken on an ERS-200 spectrometer (Academy of Sciences of the G.D.R., Berlin) working in the X-band with 100 kHz magnetic modulation. The magnetic field was measured with a MJ-110 R magnetometer (Radiofau, Poland), and the microwave frequency with a c-3-54 counter (U.S.S.R.). The standards used were DPPH (1,1-diphenyl-2-picrylhydrazyl) ($g = 2.0037 \pm 0.0002$) and $\text{Mn}^{2+}/\text{ZnS}$ ($g = 2.0024 \pm 0.0003$; $A = -0.00640 \text{ cm}^{-1}$). The samples were irradiated with an HBO 200 W arc (Narva, Berlin) directly in the resonator cavity.

RESULTS AND DISCUSSION

The effects of $\text{VO}(\text{II})$, $\text{Co}(\text{III})$, and $\text{Fe}(\text{III})$ 2,4-pentanedionates on the photolysis of $t\text{-BuOOH}$ in benzene and toluene can be seen from Figs 1 and 2, respectively. The presence of $[\text{VO}(\text{acac})_2]$ and $[\text{Co}(\text{acac})_3]$ in both solvents results in significant

increases in the rate of photochemical decomposition of *t*-BuOOH compared with *t*-BuOOH alone. In contrast to this, $[\text{Fe}(\text{acac})_3]$ reduces the rate of *t*-BuOOH photolysis. This inhibiting effect is quite unexpected, since in previous studies marked catalytic and photocatalytic effects of $[\text{Fe}(\text{acac})_3]$ were observed in thermal and photochemical oxidations of benzaldehyde¹⁶, ethyl benzene⁵, and tetraline^{4,6}. To explain the inhibiting effect and to give a mechanistic interpretation of the photocatalytic effects of VO(II) and Co(III) 2,4-pentanedionates, we need to know the amounts of radiation absorbed by individual components of the reaction solution. Fig. 3 shows absorption spectra of benzene solutions of *t*-BuOOH, $[\text{VO}(\text{acac})_2]$, $[\text{Co}(\text{acac})_3]$, and $[\text{Fe}(\text{acac})_3]$. In the presence of $[\text{Fe}(\text{acac})_3]$ and $[\text{Co}(\text{acac})_3]$, almost all the absorbed radiation is taken up by the Fe(III) and Co(III) complexes, with practically no absorption by *t*-BuOOH. The absorption by $[\text{VO}(\text{acac})_2]$ increases markedly for wavelengths shorter than 340 nm, and in this region, i.e. for 297 nm, 303 nm, 313 nm, and 334 nm lines of the high-pressure mercury arc, it also exceeds the absorption by *t*-BuOOH. The absorption of the most intense line (365 nm) by $[\text{VO}(\text{acac})_2]$ is very weak, the absorbance being comparable to that of *t*-BuOOH. The observed differences between the effects of the above 2,4-pentane-

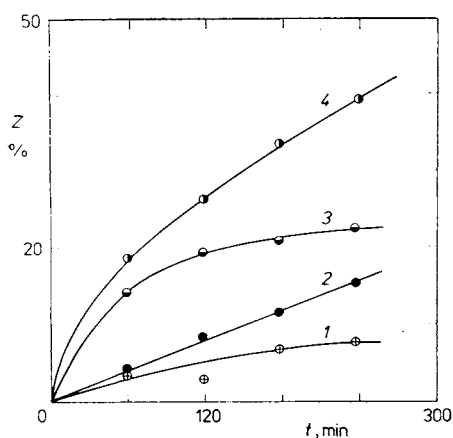


FIG. 1

Photolysis of *t*-BuOOH in benzene. A plot of Z (percentage of decomposed peroxo groups) vs time. Irradiated by the whole spectrum of an HBO 500 W arc; $T = 298 \text{ K}$; $[\text{t-BuOOH}]_0 = 0.1 \text{ mol dm}^{-3}$; $c([\text{M}(\text{acac})_n]) = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$. Added compound: 1 $[\text{Fe}(\text{acac})_3]$, 2 no addition, 3 $[\text{Co}(\text{acac})_3]$, 4 $[\text{VO}(\text{acac})_2]$

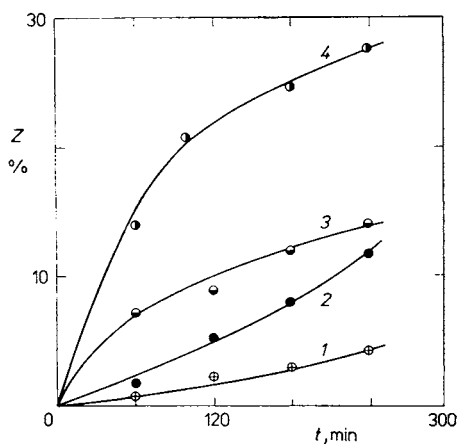


FIG. 2

Photolysis of *t*-BuOOH in toluene. A plot of Z (percentage of decomposed peroxo groups) vs time. Irradiated by the whole spectrum of an HBO 500 W arc; $T = 298 \text{ K}$; $[\text{t-BuOOH}]_0 = 0.1 \text{ mol dm}^{-3}$; $c([\text{M}(\text{acac})_n]) = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$. Added compound: 1 $[\text{Fe}(\text{acac})_3]$, 2 no addition, 3 $[\text{Co}(\text{acac})_3]$, 4 $[\text{VO}(\text{acac})_2]$

dionates on the photolysis of *t*-BuOOH indicate that the catalytic effect does not involve a simple energy transfer (sensitization), but is associated with photochemical conversion of 2,4-pentanedionates, this process being strongly dependent on the nature of the central transition metal ion.

The retarding effect of $[\text{Fe}(\text{acac})_3]$ on the photolysis of *t*-BuOOH can be explained as a result of $[\text{Fe}(\text{acac})_3]$ acting as an internal filter of photolytically active radiation and also interacting with the free radicals formed to yield more stable coordinated radicals. The absence of a photocatalytic effect of $[\text{Fe}(\text{acac})_3]$ indicates that in no case does photochemical reduction of Fe(III) to Fe(II) take place in the reaction solution for, were this to occur, the Fe(II) would doubtlessly catalyze the decomposition of *t*-BuOOH. The lack of Fe(III) reduction is in accord with results of Gafney and co-workers¹⁷, who have shown that the photoreduction of Fe(III) 1,3-diketonates strongly depends upon the solvent used and that benzene is a solvent in which it almost does not occur.

Next, we investigated EPR spectra of reaction solutions containing $[\text{VO}(\text{acac})_2]$. For comparison, we also measured the spectra without any added catalyst and with

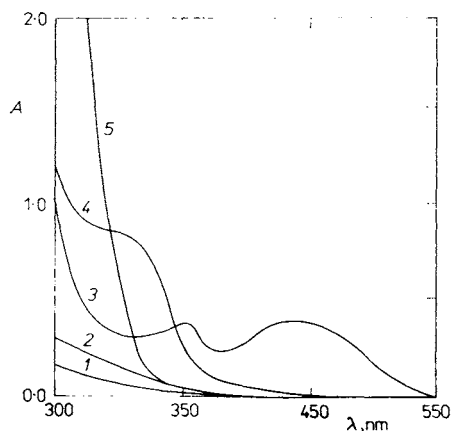


FIG. 3

Absorption spectra. 1 benzene; 2–5 benzene solutions: 2 0.1 mol dm^{-3} *t*-BuOOH, 3 $1.10^{-3} \text{ mol dm}^{-3}$ $[\text{Fe}(\text{acac})_3]$, 4 $1.10^{-3} \text{ mol dm}^{-3}$ $[\text{Co}(\text{acac})_3]$, 5 $1.10^{-3} \text{ mol dm}^{-3}$ $[\text{VO}(\text{acac})_2]$, 1 cm cell

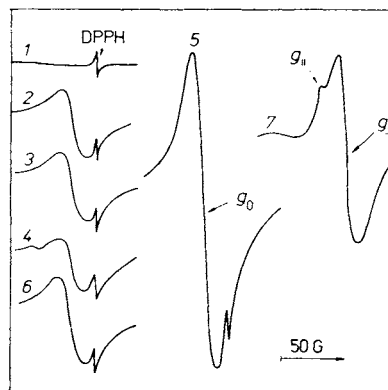


FIG. 4

EPR spectra of 0.1 mol dm^{-3} *t*-BuOOH in benzene (1–6) and toluene (7); *T*: 298 K (1–6) and 77 K (7); irradiated by the whole spectrum of an HBO 200 W arc; concentration of added 2,4-pentanedionate, $1.10^{-3} \text{ mol dm}^{-3}$. Irradiation time, s; added compound: 1 0; 0, 2 30; 0, 3 30; Fe(III), 4 0; VO(II), 5 30; VO(II), 6 1 800; VO(II), 7 3 600; VO(II)

the addition of the inhibiting $[\text{Fe}(\text{acac})_3]$. As seen in Fig. 4 showing typical EPR spectra, a solution of t-BuOOH alone (curve 1) produces no EPR signal at room temperature (298 K). After irradiating the solution with an HBO 200 W arc, an EPR signal with $g = 2.0152 \pm 0.0005$ due to free radical formation was observed (curve 2). The free radical intermediate formed by photolysis of t-BuOOH is probably $(\text{CH}_3)_3\text{COO}^*$, which is known to be little sensitive to dioxygen. The radicals $(\text{CH}_3)_3\text{C}^*$ and $(\text{CH}_3)_3\text{CO}^*$ should, according to generally accepted concepts², react very rapidly with oxygen. In addition, the measured value $g = 2.0152$ is in good agreement with that given in the literature¹⁸ for RO_2^* free radicals.

Curve 4 in Fig. 4 shows that t-BuO₂^{*} is also formed by thermal reaction of $[\text{VO}(\text{acac})_2]$ with t-BuOOH. Irradiation of the solution results in a further increase in the rate of t-BuO₂^{*} formation (curve 5). However, the rapid increase in the concentration of t-BuO₂^{*} is relatively soon followed by a gradual decrease (curve 6). These changes are discussed in greater detail below. The EPR signal of an irradiated frozen solution of t-BuOOH and $[\text{VO}(\text{acac})_2]$ is characterized by curve 7. Unlike $[\text{VO}(\text{acac})_2]$, $[\text{Fe}(\text{acac})_3]$ causes no increase in the concentration of t-BuO₂^{*} (curve 3).

The EPR technique was also used to monitor concentration changes of $[\text{VO}(\text{acac})_2]$ alone when irradiated in solution at room temperature (Fig. 5). In the absence of

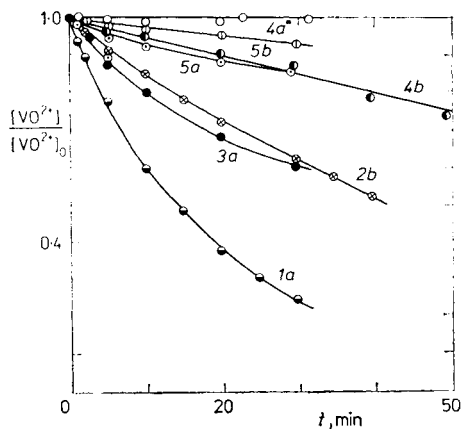


FIG. 5

Concentration change of $[\text{VO}(\text{acac})_2]$ in toluene (a) and benzene (b) during irradiation with an HBO 200 W arc in the air and an inert atmosphere of argon (*) in the absence of t-BuOOH; $T = 298 \text{ K}$; $[\text{VO}(\text{acac})_2]_0$ concentration, mol dm^{-3} : 1 $2.5 \cdot 10^{-4}$, 2 $4 \cdot 10^{-4}$, 3 $5 \cdot 10^{-4}$, 4 $1 \cdot 10^{-3}$, 5 $2 \cdot 10^{-3}$

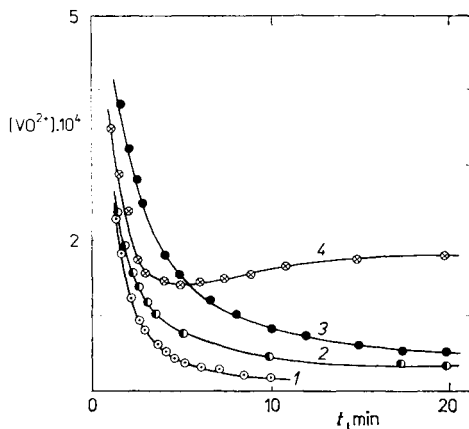


FIG. 6

Thermal reaction of $[\text{VO}(\text{acac})_2]$ with t-BuOOH in the air (1, 3) and in an argon atmosphere (2, 4); $T = 298 \text{ K}$; $c([\text{VO}(\text{acac})_2]) = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$; $[\text{t-BuOOH}]_0$, mol dm^{-3} : 1 $2 \cdot 10^{-3}$, 2 $1 \cdot 10^{-3}$, 4 $9 \cdot 10^{-4}$

oxygen from the air, UV radiation had no measurable effect on the intensity of EPR signal from $[\text{VO}(\text{acac})_2]$ over the time period of measurement. This is in accord with previously reported stability of $[\text{VO}(\text{acac})_2]$ towards UV radiation: the expected CTTS was not observed for the complex alone¹⁷. On irradiation in the presence of oxygen, however, vanadyl is photochemically oxidized to the diamagnetic $\text{V}(\text{V})$. Fig. 5 confirms that the rate of VO^{2+} oxidation is controlled photochemically, by the amount of absorbed quanta. The higher the initial concentration of $[\text{VO}(\text{acac})_2]$, the smaller the relative concentration change $[\text{VO}^{2+}]/[\text{VO}^{2+}]_0$. This behaviour was observed in both benzene and toluene solutions.

Fig. 6 demonstrates that in the presence of $t\text{-BuOOH}$ oxygen is not necessary even for disappearance of the EPR signal from $[\text{VO}(\text{acac})_2]$ by the thermal reaction and that the reaction of $[\text{VO}(\text{acac})_2]$ with $t\text{-BuOOH}$ follows essentially a one-to-one stoichiometry.

In further experiments, we investigated the kinetics of $(\text{CH}_3)_3\text{CO}_2^\cdot$ formation. The concentration of the free radical was expressed as the ratio of measured EPR signal produced by the free radical to EPR signal of a standard. Fig. 7 shows a plot of the concentration of the free radical formed on irradiation of frozen $t\text{-BuOOH}$ solutions (77 K) as a function of time. It is seen that the free radical species accumu-

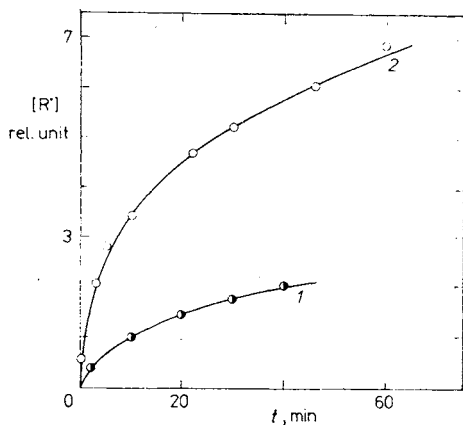


FIG. 7

Variation in free radical concentration ($g = 2.0152$) with time for irradiation of 0.1 mol dm^{-3} solution of $t\text{-BuOOH}$ in toluene by the whole spectrum of an HBO 200 W arc; $T = 77 \text{ K}$; 1 no addition, 2 $c([\text{VO}(\text{acac})_2]) = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$

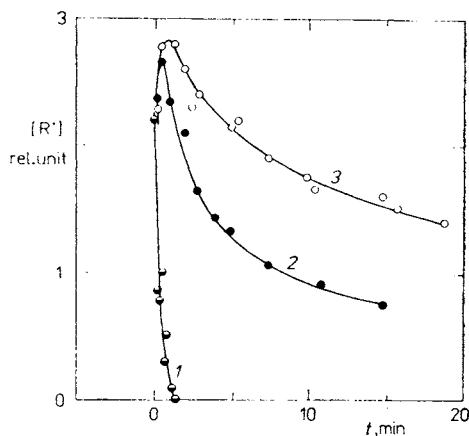


FIG. 8

Variation in free radical concentration ($g = 2.0152$) with time for irradiation of 0.1 mol dm^{-3} solution of $t\text{-BuOOH}$ in benzene by the whole spectrum of an HBO 200 W arc; $T = 298 \text{ K}$; 1, 2 no addition (1 irradiation interrupted after 1 min), 3 $c([\text{Fe}(\text{acac})_3]) = 1 \cdot 10^{-3} \text{ mol dm}^{-3}$

late in frozen solutions and that markedly higher free radical concentrations are produced in the presence of $[\text{VO}(\text{acac})_2]$. This finding indicates that the photocatalytic effect of $[\text{VO}(\text{acac})_2]$ is to enhance free radical formation in the primary photochemical process. It also suggests that, in frozen solutions at least, t-BuOOH enters the coordination sphere of vanadium. The complex $[\text{VO}(\text{acac})_2 \dots \text{ROOH}]$ may also be expected to exist in solution.

The time dependence of the concentration of t-BuO₂ free radicals at room temperature in a solution without added photocatalyst is represented in Fig. 8. On irradiation of the reaction mixture, there is a very rapid increase in t-BuO₂ concentration, but starting from the first minute of irradiation a gradual decrease is observed. On termination of irradiation, the EPR signal from the radical disappears very rapidly (within one minute). This is not surprising, since t-BuO₂ is sufficiently reactive. An interesting result is, however, the gradual decrease in t-BuO₂ concentration (following a steep increase) under continuous irradiation. In no case does this decrease correspond to an overall reduction of t-BuOOH concentration in the reaction solution (see Figs 1 and 2), but is apparently due to a reduction in ROOH concentration within the irradiated photochemically active layer of solution in the cell of the EPR resonator. The cell is too narrow to allow effective mixing to even out the concentration gradient of decomposed t-BuOOH and hence of t-BuO₂ radicals. The reduction in t-BuO₂ concentration may partly be brought about by the photolytic radiation itself, which may accelerate reactions of t-BuO₂ termination. This idea gains support from the reaction in the presence of $[\text{Fe}(\text{acac})_3]$, where a slower decrease in t-BuO₂ concentration is observed (Fig. 8, curve 3); $[\text{Fe}(\text{acac})_3]$ acts here as an internal filter of the photolytically active radiation.

Fig. 9 shows a plot of the concentration of t-BuO₂ formed by t-BuOOH photolysis in the presence of $[\text{VO}(\text{acac})_2]$ as a function of time. By comparing Figs 8 and 9,

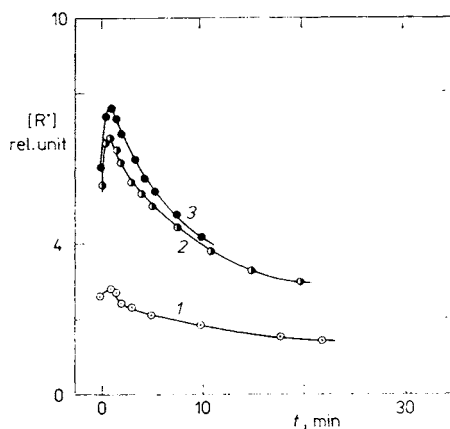
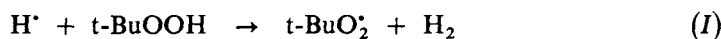
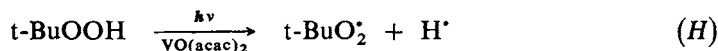


FIG. 9

Variation in free radical concentration ($g = 2.0152$) with time for irradiation of 0.1 mol dm^{-3} solution of t-BuOOH in the presence of $1 \cdot 10^{-3} \text{ mol dm}^{-3} [\text{VO}(\text{acac})_2]$ by the whole spectrum of an HBO 200 W arc in toluene (1) and benzene (2, 3) in the air (1, 2) and an inert atmosphere of argon (3); $T = 298 \text{ K}$

it is evident that $[\text{VO}(\text{acac})_2]$ significantly increases the concentration of t-BuO_2^\cdot . From Fig. 9 oxygen is seen to have no appreciable effect on the kinetics of t-BuO_2^\cdot formation. This means that the free radical is produced either directly by photodissociation of t-BuOOH (reactions (H) and (I))



or by photodissociation of t-BuOOH to t-BuO^\cdot and OH^\cdot followed by interaction of the two free radicals still within the coordination sphere of vanadium or the solvent cage (reaction (J) followed by (I))

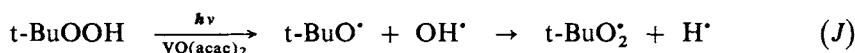


Fig. 9 also shows that the concentration of t-BuO_2^\cdot in benzene solution is much higher (by a factor of about two) than that in toluene solution. This difference corresponds with the experimentally observed higher rate of t-BuOOH photolysis in benzene. Clearly, the recorded EPR signal from t-BuO_2^\cdot corresponds to the actual intermediate of the photochemical decomposition of *t*-butyl hydroperoxide.

The results obtained confirm the assumption that transition metal compounds may affect the photolysis of t-BuOOH , either by accelerating ($[\text{VO}(\text{acac})_2]$, $[\text{Co}(\text{acac})_3]$) or retarding the reaction ($[\text{Fe}(\text{acac})_3]$). Apparently, there is no direct relationship between catalysis of photochemical decomposition of hydroperoxides and catalysis of photoinitiated oxidation of hydrocarbons by dioxygen. $[\text{Fe}(\text{acac})_3]$ catalyzes a number of photoinitiated oxidations⁴⁻⁶, but retards the photolysis of t-BuOOH . This also implies that a catalyst may take part not only in the initiation of oxidation, but also in propagation steps. This confirms the assumption¹⁹ that a catalyst may participate in all stages of an oxidation process.

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