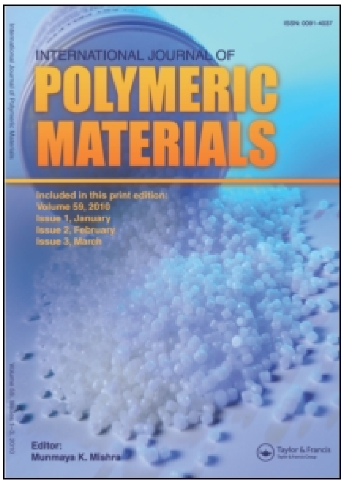

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Influence of Chromium(III) Ions Photochemical Decomposition of *t*-Butylhydroperoxide

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The presence of chromium(III) in form of acetylacetonate increases the quantum yield of *t*-butylhydroperoxide photolysis in benzene solutions at 300–400 nm.

So, the 0.2 M hydroperoxide solution containing 0.0005 M chromium(III) acetylacetonate exhibits the quantum yield of photolysis which is cca 25 times higher than that of hydroperoxide alone. The phenomenon is explained in terms of peroxy-radicals coordinated in the ligand field of metal ion.

KEYWORDS: Photodegradation, acetylacetonate of chromium(III), t-butylhydroperoxide, yield, peroxyradicals, ligands

INTRODUCTION

Relatively low photooxidative stability of polyolefins is one of the limiting factors of their wider use. It is well known that hydroperoxides are the primary products of thermo- and photooxidative processes taking place in hydrocarbons and also in polyolefins.[1] In the latter there are always traces of metals present, predominantly in form of catalyst residues—namely Ti, Cr, Al, V. The polymer may become further contaminated by metallic impurities during the application (Cu).

The detrimental effect of transition metal ions upon the polyolefin stability has been well known. Most frequently, this effect is attributed to redox reaction of metal ions in the presence of hydroperoxides, causing the decomposition of the latter[2] (Eqs. (1), (2)):

$$Me^{n+} + ROOH \rightleftharpoons [Me \ldots ROOH]^{n+} \rightarrow Me^{n+1} + RO^{\cdot} + OH^{-} \qquad (1)$$

$$Me^{n+1} + ROOH \rightleftharpoons [Me \ldots ROOH]^{n+1} \rightarrow Me^{n+} + ROO^{\cdot} + H^{+} \qquad (2)$$

These reactions have been studied to some detail for a number of metals and hydroperoxides, the attention being focused to the thermally induced

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decomposition.[3] Relatively little is known, however, about the photooxidative stability of polymers in connection with the presence of catalytic impurities.[4,5] The influence of metals on the photolysis of organic hydroperoxides has not practically been given attention.[6] For this reason we examined the photochemical decomposition of tert-butyl hydroperoxide (TBHP) in the presence of chromium(III) acetylacetonate—$Cr(acac)_3$.

EXPERIMENTAL

The irradiation runs were carried out on an optical train of our own design. The light of a Xe-lamp was filtered off to obtain a 300–400 nm band. The intensity of light flux monitored by a Rhodamin B quantum counter whose spectral response was calibrated by a pyroelectric detector (Laser Precision Corp.) and a Schoeffel GM 250 grating monochromator. The UV spectra were taken on a CF 4 Optica Milano spectrometer. The glc analyses were carried out on an F 11 Perkin–Elmer gas chromatograph while all ESR experiments were done using a Bruker ER 200 E/T-SRC instrument.

The study was carried out in benzene purified by several freeze-thaw processes. tert-Butylhydroperoxide synthetized according to[7] was purified by preparative gas chromatography on an all glass apparatus. The purity better than 98.5% was achieved. Chromium(III) acetylacetonate was obtained from Institute of Inorganic Chemistry, Prague and was used without further purification, Typically 0.05–0.25 M hydroperoxide solutions containing $0.4–5 \times 10^{-4}$ M $Cr(acac)_3$ were irradiated. The extent of reaction was followed through the formation of tert-butyl alcohol (TBA) analysed by glc.

RESULTS AND DISCUSSION

Pure TBHP photolysis

Figure 1 shows a typical dependence of TBA formation on time when irradiating at various initial concentrations of TBHP. Out of the initial slopes, the photolysis rates could be calculated. From the spectral characteristics of the photochemical equipment and the absorption curve of TBHP in benzene it was possible to calculate the amount of light absorbed by TBHP within 300–400 nm and eventually the quantum yield of TBA formation during TBHP photolysis (Table I). Since TBA represents 80–95% of products formed during TBHP photodecomposition it is safe to assume that its quantum yield of formation truly reflects the extent of hydroperoxide photolysis.

As shown in Table I the quantum yield of TBA formation is 0.75 ± 0.02 over the concentration range of our experiments. This indicates that the decomposition of hydroperoxide under these conditions proceeds with the quantum efficiency close to unity. Norrish *et al.*[8] as well as Zahradnickova *et al.*[9] who photolysed

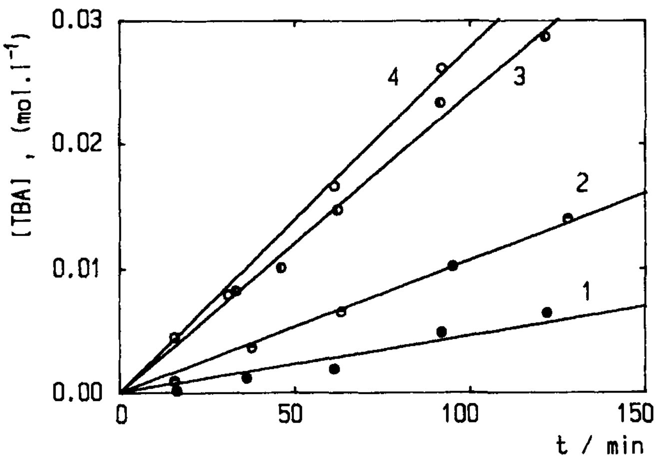


FIGURE 1 TBA formation during photolysis of TBHP in benzene at 25°C $[TBHP]_0$ in mol l^{-1}: 1 – 0.05, 2 – 0.09, 3 – 0.19, 4 – 0.26.

TBHP in non-polar solvents reported the quantum yields somewhat higher (3.5–6.0). The latter authors put forward the hypothesis according to which the polar TBHP molecules tend to form hydrogen-bonded clusters in non-polar medium. When excited by the absorption of photon, the RO$^\cdot$ and $^\cdot$OH radicals are formed by peroxidic bond scission. These radicals then readily attack the hydroperoxide molecules within the cluster, thus promoting the chain decomposition.

In benzene the formation of hydrogen bonded associates between two or more TBHP molecules is suppressed by a competing process of the complex formation between hydroperoxide and aromatic solvent.[10] The IR spectra of TBHP solutions in benzene exhibit a shift of monomeric O—H due to hydroperoxide from 3512 cm^{-1} (found in CCl_4) to 3485 cm^{-1}. In the case of 0.2 M solution it was calculated that ca 80% hydroperoxide is bonded in a complex with benzene. It seems likely that the π-complex of ROOH with benzene enables the efficient relaxation of primarily formed RO$^\cdot$ and $^\cdot$OH radicals and their recombination in the solvent cage. Only those radicals which escape participate in chain decom-

TABLE I

Reaction rates of TBA formation (w), absorbed light intensity by TBPH (I_A) and quantum yields of TBA formation (ϕ) during photolysis of TBHP in benzene at 25°C by 300–400 nm light

$\frac{[TBHP]_0}{mol\,l^{-1}}$	$\frac{10^6(I_A)}{E\,l^{-1}\,s^{-1}}$	$\frac{10^6(w)}{mol\,l^{-1}\,s^{-1}}$	ϕ
0.05	1.29	0.94	0.73
0.09	2.31	1.75	0.76
0.19	4.58	3.51	0.77
0.26	6.48	4.71	0.73

position of hydroperoxide. This would account for the observed lower quantum yield of TBHP decomposition in benzene.

Photolysis of TBHP in the presence of Cr(acac)$_3$

When irradiating in the presence of Cr(acac)$_3$ the situation may become somewhat complicated due mainly to the following factors:

i) A possible thermal decomposition of hydroperoxide induced by the presence of chromium ions.

ii) A relatively strong absorption of Cr(acac)$_3$ which substantially reduces the amount of light received by hydroperoxide.

As to i) it may be concluded that no measurable decomposition of TBHP in the presence of Cr(acac)$_3$ occurs at 25°C within the first 12 hours. After elapsing of this period a slow thermal decomposition of hydroperoxide starts but its maximal rate is by two orders of magnitude lower than that measured during the photolysis.

As to the second point the light intensity received by TBHP in the presence of Cr(acac)$_3$ had to be computed using the absorption characteristics of both components and the emission characteristics of the light source for the 300–400 nm region. Figure 2 shows the extent of screening of TBHP due to the presence of Cr(acac)$_3$. The results of irradiation are summarised in Table II. It follows that in the presence of Cr(acac)$_3$ higher rates of TBA formation are observed in spite of the fact that much less light was received by hydroperoxide than in the absence of Cr(III)complex.

Consequently, higher quantum yields of TBA formation are found when irradiating the hydroperoxide in the presence of Cr(acac)$_3$. As shown in Table II its value may increase as much as 26 times with regard to photolysis in the absence of metal complex.

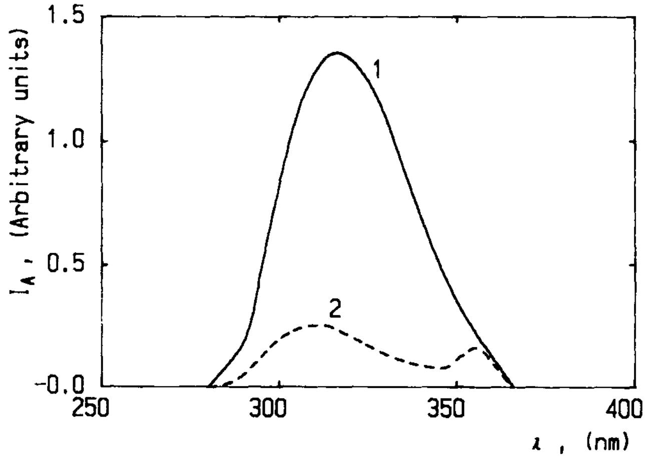


FIGURE 2 Intensity of light received by 0.2 M TBHP (I_A) in the absence (curve 1) and in the presence of 2×10^{-4} M Cr(acac)$_3$ (curve 2).

TABLE II

Reaction rates of TBA formation (w), absorbed light intensity by TBHP (I_A) and quantum yields of TBA formation (ϕ) at various concentrations of $Cr(acac)_3$ during photolysis of 0.2 M TBHP in benzene at 25°C by 300–400 nm light ($I_0 = 1 \times 10^{-3}\,E\,l^{-1}\,s^{-1}$)

$10^4(Cr(acac)_3)$ mol l^{-1}	$10^6(q)$ mol $l^{-1}\,s^{-1}$	$10^6(I_A)$ E $l^{-1}\,s^{-1}$	ϕ
0.0	3.51	4.58	0.8
0.4	4.02	2.51	1.6
0.6	4.10	2.02	2.0
0.8	4.27	1.68	2.5
1.0	7.22	1.45	5.0
2.0	9.45	0.90	11.0
2.7	9.98	0.76	13.0
4.0	8.59	0.60	14.3
5.2	13.70	0.52	26.4

ESR measurements

The irradiations were carried out directly in the cavity of ESR instrument using a high pressure Hg-lamp with a Simax glass filter. During the experiments both with hydroperoxide alone and in the presence of $Cr(acac)_3$ it was possible to observe a characteristic singlet ($g = 2.015$) with peak-to-peak width 1.5 mT which we interpret as a signal due to $ROO^{\cdot}$ radicals.[2]

The behavior of peroxy radical signal during both continuous and intermittent irradiation is however worth noting (see Figure 3). When hydroperoxide alone is irradiated in benzene a rapid increase of peroxy radical signal intensity is observed but its value decreases steadily with time. When the light is switched off the signal disappears immediately and reappears only when the light is switched on again. When $Cr(acac)_3$ is present in the system being irradiated the intensity increase is somewhat slower but the final signal level is 2–3 times higher than in the case of pure hydroperoxide. Moreover, this level remains constant for the whole duration of experiment. Upon switching off the light source no complete disappearance of signal is seen, unlike in the previous case.

These observations are in accordance with the data reported recently by Negishi *et al.*[6] who photolysed TBHP in the presence of $FeCl_3$. The ESR spectral data allowed them to conclude that $FeCl_3$ strongly enhances the formation of peroxy radicals. The mechanism put forward by these authors could hardly account for the prolonged lifetime of peroxy radicals as observed in this study. This phenomenon may however be explained in terms of radical coordination in the legand field of metal. This was first suggested by Tkáč and co-workers[11–13] who have obtained evidence from ESR studies that transition metal chelates react to form stable complexes in which alkylperoxy radicals are coordinated to the metal atom; for example:

$$Cu(acac)_2 + 2ROOH—ROH + [Cu(acac)_2RO_2]^+OH^- \qquad (3)$$

The stability of such complexes has been reported to be so great, that no decrease

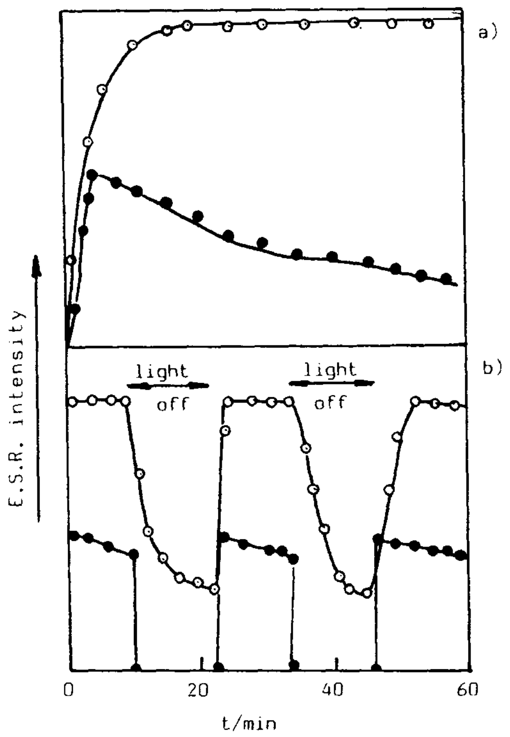


FIGURE 3 ESR signal intensity dependence on irradiation time during the photolysis of 0.1 M TBHP solutions in benzene in the presence (○) and absence (●) of Cr(acac)$_3$ (0.01 M). a) continuous irradiation, b) intermittent irradiation.

in the radical concentration is found when the complex of tert-butylperoxy radicals with cobalt acetylacetonate is stored, in solution at 0°C, for 2 weeks.

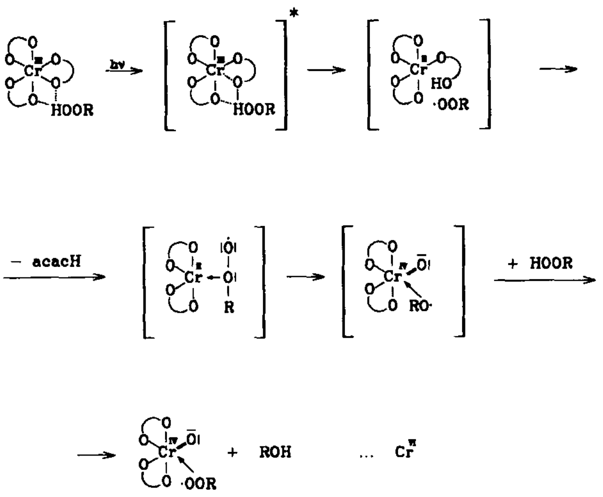
The formation of Cr(III) coordinated tert-butylperoxy radicals in our case is suggested to proceed in the following way (see Scheme 1).

During the photolysis of the system acetylacetonate-hydroperoxide two main processes take place: i) direct photolysis of hydroperoxide, ii) decomposition of TBHP in the vicinity of the ligand field of metal. The absorption of light quantum weakens the bonding metal–ligand. If neither hydroperoxide nor other hydrogen donating compound is present an efficient relaxation of this exicted state takes place and the quantum yield of acetylacetonate decomposition approaches zero. This is in accordance with our experiments with the photolysis of Cr(acac)$_3$ solutions carried out without hydroperoxide and also with the literature data.[14]

When however a hydrogen donor, such as hydroperoxide, is present a homolytic splitting of metal–oxygen bond occurs, followed by hydrogen abstraction from hydroperoxide. The protonated acetylacetonate ligand is given up in the form of neutral molecule. The peroxy radical thus formed remains in the coordination sphere of metal.

The second step is visualised as the oxidative addition during which the peroxidic bond is broken leading to the formation of Cr(IV) coordinated alkoxy

$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO}\cdot + \cdot\mathrm{OH}$$



SCHEME 1

radical. The latter being substantially more reactive will abstract readily hydrogen from other hydroperoxide molecule giving rise to a new peroxy radical. A subsequent insertion of this radical into the ligand field of metal and a repetition of the whole process will lead to a successive exchange of all ligands and to the oxidation of metal to Cr(VI). The resulting chromium trioxide is soluble in benzene solution of TBHP. It forms a purple-pink solution whose spectrum in UV and visible corresponds to color changes observed during the irradiation of actual samples. Also the benzidine test confirmed qualitatively the presence of Cr(VI) in the reaction mixture.

CONCLUSION

The enhancement of TBHP quantum yield during its photolysis in the presence of $Cr(acac)_3$ is attributed to the coordination of alkoxy and alkylperoxy radicals in the ligand field of Cr. In this way the level of radicals in the system being irradiated is substantially higher the consequence of which is the promotion of the induced hydroperoxide decomposition.

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