

Study of the quenching of triplet carbonyl groups and singlet oxygen by light stabilizers

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The quenching constants of triplet carbonyl groups and singlet oxygen have been measured in model systems for nine light stabilizers of the type of organic ultraviolet absorbers and metal chelates as well as six acetylacetonates with bivalent and trivalent ions. Confrontation of the values of quenching constants has shown that organic ultraviolet absorbers are effective quenchers of triplet carbonyl groups and poor quenchers of singlet oxygen. Nickel(II) chelates are poor quenchers of triplet carbonyl groups and effective quenchers of singlet oxygen.

The feasibility of applying the results obtained with model systems to the photooxidation of polypropylene is discussed.

The evaluation of light stabilizers from the physicochemical viewpoint has not been hitherto sufficiently elaborated. The tests of accelerated and outdoor ageing by which the standard stabilization systems as well as the newly developed systems are examined represent a very complex process which gives information about overall efficiency. But in this process it is not possible to separate the individual functions of light stabilizers. The additional physicochemical measurements are concentrated mainly on absorption spectra. These measurements provide valuable information on the efficiency of a given light stabilizer functioning as a light filter. However, such measurements are necessary for a more complete understanding, which characterize light stabilizers as quenchers of the excited states of chromophores, playing an important part at the beginning or during photooxidative degradation, quenchers of singlet oxygen, inhibitors of secondary reactions, etc.

The existence of a non-screening mechanism of light stabilizers was evoked especially in connection with their use in thin films and fibers [1—3]. Under these conditions their overall protective efficiency is higher than it should be according to their screening. Though the photooxidative degradation of polymers shows many common features, every type of polymer has specific properties. It follows from this fact that the stabilization system itself has to be chosen with respect to polymer substrate. Among the polymers used commercially, poly- α -olefins, in particular polypropylene, show a low light stability. Poly- α -olefins are polymers with saturated carbon chains which, as shown by the model low-molecular hydrocarbons, do not absorb in the ultraviolet region of solar radiation and thus they could exhibit a high light stability. As a matter of fact, they are very sensitive to photooxidative ageing. The initiating mechanism of photo-

oxidative degradation is still a subject of controversy. The residues of metal catalysts [1-3], carbonyl and hydroperoxide groups formed during thermal treatment [1-3], and charge transfer complexes between polymer and oxygen [3, 4] are assumed to be responsible for photooxidation. The initiating mechanism has not hitherto been cleared up and is likely to remain incompletely elucidated till sufficiently sensitive methods for the detection of defects in the structure of polymers and investigation of chemical reactions on these defects are available. It may, however, be supposed that carbonyl groups play an important role during photooxidation. A possible quenching of the excited carbonyl groups of polypropylene by light stabilizers was assumed by *Pivovarov* and *Lukovnikov* [5] on the basis of quenching the luminescence of polypropylene at liquid nitrogen temperature by the derivatives of 2-hydroxybenzophenone and 2-(2'-hydroxyphenyl)benzotriazole. The results obtained until now by studying the quenching of photolysis and photooxidation of polymers as well as characterizing the light stabilizers as quenchers were summarized in a review by *Klöpper* [6].

The evaluation of the quenching efficiency of light stabilizers of the type of 2-hydroxybenzophenone and 2-(2'-hydroxyphenyl)benzotriazole in polypropylene has shown that the derivatives of 2-hydroxybenzophenone are quenchers of the excited triplet dialkyl carbonyl groups during photooxidation while the derivatives of 2-(2'-hydroxyphenyl)benzotriazole are not operative as quenchers in this case [7, 8]. On the other hand, it has been demonstrated that the derivatives of 2-(2'-hydroxyphenyl)benzotriazole are quenchers of the triplet aryl carbonyl groups in polymers and low-molecular compounds as well [9, 10]. Therefore *Guillory* and *Cook* [10] suppose that some steric hindrances of energy transfer manifest themselves in polypropylene films in the case of the derivatives of 2-(2'-hydroxyphenyl)benzotriazole.

There are inconsistent experimental results and opinions on the mechanism of the efficiency of some metal chelates developed recently [1-3]. *Briggs* and *McKellar* [11, 12] have assumed on the basis of the quenching of anthracene in flash photolysis that these compounds may be regarded as quenchers of carbonyl groups. The quenching of the triplet states of aromatic hydrocarbons and benzophenone was thoroughly studied by *Adamczyk* and *Wilkinson* [13]. On the other hand, it was found by investigating the photolysis of carbonyl polymers in films [9] as well as some carbonyl model compounds [14] that nickel(II) chelates are quenchers of low efficiency.

In addition to light stabilizers the excited carbonyl groups may be quenched by oxygen which is an effective triplet and singlet quencher because of its paramagnetic molecules. *Trozzolo* and *Winslow* [15] suggested that singlet oxygen might play an important role in the photodegradation of polyolefins. But they substantiated this suggestion neither by a qualitative evidence of singlet oxygen in the polymers with carbonyl groups formed during photooxidation or built in polymer nor by quantitative data on the amount of the singlet oxygen formed, its reactivity or lifetime in polymer. Part of these data was compiled by *Kearns* and co-workers who demonstrated that the quenching of the excited carbonyl groups resulted in the formation of singlet oxygen [16], the lifetime of which depended considerably on the environment [17, 18]. In the nonpolar environment of carbon tetrachloride its lifetime is about 50 times longer than it is in water.

The Trozzolo hypothesis of the role of singlet oxygen as well as the high efficiency of nickel(II) compounds and derivatives of piperidine (though they absorb slightly in the near u.v. region) caused the light stabilizers to be tested as inhibitors in the reactions of the singlet oxygen which was generated either chemically or physically. Confrontation of the results obtained with the quenching of the singlet oxygen generated by several

chemical methods and radio-frequency discharge led in the case of the derivatives of piperidine [19] and nickel(II) chelates [20] to the conclusion that these substances are quenchers of singlet oxygen. The reaction of rubrene as a substrate with singlet oxygen was used for testing the light stabilizers as singlet oxygen quenchers. The singlet oxygen was generated by methylene blue as a sensitizer [21], rubrene itself [22], or low-frequency discharge [23]. It was demonstrated that in the case of nickel(II) chelates the quenching and stabilizing efficiencies were in correlation [22, 23]. The quenching efficiency of nickel(II) chelates was also demonstrated by the measurements of flash photolysis [24].

The aim of this study is to confront the results obtained with the quenching of carbonyl groups by light stabilizers in a model polymer [9] with the results obtained with the quenching of singlet oxygen in a model system and judge the suitability of these models to describe the efficiency of light stabilizers in the photooxidation of polypropylene.

Experimental

Light stabilizers: *p*-*tert*-butylphenylsalicylate, 2-hydroxy-4-methoxybenzophenone, 2-hydroxy-4-*n*-octyloxybenzophenone, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(2'-hydroxy-3'-chloro-5'-*tert*-butylphenyl)benzotriazole and metal chelates: nickel(II) bis[2,2'-thiobis(4-*tert*-octyl)phenolate], nickel(II) *n*-butylamine-2,2'-thiobis(4-*tert*-octyl)phenolate, nickel(II) bis(butyl-3,5-di-*tert*-butyl-4-hydroxybenzyl)phosphate were commercial products.

Nickel(II) *p*-*tert*-butylphenylsalicylate was prepared from *p*-*tert*-butylsalicylate and nickel(II) chloride in sodium methylate according to [25]. M.p. 229–230°C.

For $C_{34}H_{34}O_6Ni$ calculated: 9.86% Ni; found: 10.1% Ni.

Table 1

Metal chelates

Metal	Chemical	Medium	Solvent for crystallization	M.p. [°C]		Calculated/ found % Ni	Ref.
				Ref.	Found		
Nickel(II)	Ni(OH) ₂	Benzene	Ethanol	228 ^a	225–226	22.8 22.3	[26, 28]
Cobalt(II)	Co(OH) ₂	Chloroform	Sublimed (80°C/1 torr)			22.9 22.3	[26, 29]
Zinc(II)	Zn(NO ₃) ₂	Ammonia	Benzene	130 ^a	129–130	24.7 24.7	[26]
Copper(II)	Cu(CH ₃ COO) ₂	Water	Chloroform	230 ^a	236	24.2 25.7	[26, 28]
Iron(III)	FeCl ₃	Sodium ethylate	Ethanol	184 ^b	183–185	15.8 15.6	[27, 28]
Chromium(III)	Cr(NO ₃) ₃	Ethanol	Chloroform	216 ^b	214–215	14.9 14.8	[27]
Cobalt(III)	CoCl ₂ + H ₂ O	Ammonia	Chloroform	241 ^b	238–259	16.5 16.2	[27, 28]

a) Ref. [26].

b) Ref. [27].

The preparation of metal chelates of acetylacetone is described in literature [26–28]. In some cases some lesser modifications were performed. The initial substances were acetylacetone and a compound cited in Table 1. All melting points were measured with an apparatus "Böetius" and were not corrected. All substances were dried *in vacuo* over P_2O_5 . The structures of substances were not studied in contrast to some recent papers (*e.g.* cobalt(II) tetramer [30], nickel(II) trimer [31], copper(II) complex [32], *etc.*).

Ferrocene was the same as described in paper [9]. Naphthalene was zonally refined. β -Carotene was a product of "Léčiva", Prague. Rubrene was purchased from Aldrich—Europe, Belgium. The solvents (benzene, carbon tetrachloride, and chloroform) were of spectroscopic purity (Lachema, Brno).

Poly(vinyl phenyl ketone) was prepared as described in paper [9] and its limiting viscosity number obtained in benzene at 30°C was $[\eta] = 0.96 \text{ dl g}^{-1}$.

The polymer films for the study of quenching were prepared on a Petri dish of 4 cm diameter by weighing 0.1 g of polymer and dissolving it in 2 ml of chloroform. By slow evaporation a film was obtained. To the film thus prepared a quencher (0–5 mg) was added and another 2 ml of chloroform was put into the Petri dish. In this way the films with homogeneously dispersed quenchers were obtained. The films in Petri dishes were irradiated in a rotary apparatus. The source of radiation was a 40 W medium pressure mercury arc (HQE 40, BGW Berlin, GDR) placed in a cooling jacket. The cooling jacket was surrounded by a concentric glass cylinder providing a space of 1 cm width. This space contained a filter solution (600 g of $\text{NaBr} \cdot 2\text{H}_2\text{O}$ and 3 g of $\text{Pb}(\text{NO}_3)_2$ in 1 l of distilled water) which transmitted the radiation with the wavelength above 340 nm. The polymer absorbed the rays up to 380 nm. The liquid filter and absorption of the polymer delimited the radiation of mercury lamp with the wavelength of 366 nm as a photochemically active component. The irradiated films were dissolved in benzene and put quantitatively into a 10-ml volumetric flask so that the resulting concentration was 1 g/100 ml. The viscosity of solutions was measured with an Ubbelohde viscosimeter at 30°C.

All the operations with polymer films and solutions were carried out in yellow light.

The density of poly(vinyl phenyl ketone) determined by the method of electromagnetic float was 1.31 g cm^{-3} .

The ultraviolet absorption spectra were taken on a recording spectrophotometer Spécord UV-VIS (Zeiss, Jena). The screening effect of the investigated compounds at 366 nm was evaluated from the measurements on a single-beam nonrecording spectrophotometer VSU-1 (Zeiss, Jena).

The course of the decay of rubrene emission in aerated solutions of rubrene was investigated with a device of own construction. A 150 W xenon discharge arc was used as a source of radiation. By combining two liquid filters (500 g NaBr , 3 g $\text{Pb}(\text{NO}_3)_2$ in 1 l of distilled water, width 5 cm and 50 g K_2CO_3 , 0.384 g K_2CrO_4 in 1 l of distilled water, width 5 cm) we achieved the wavelengths of the exciting radiation exceeding 450 nm. The emitted radiation rising at a 90° angle with respect to the exciting radiation entered a monochromator SPM-2 (Zeiss, Jena) equipped with a synchronous motor and gear box of the type B-601 (Novoborské strojírny, Nový Bor) and was detected by means of a photomultiplier (EMI, 6256 B). The photomultiplier was fed by a high voltage source NBZ 411 (Tesla, Liberec). The signal of photomultiplier was amplified by a laboratory dynamic amplifier MEK 100 (Tesla, Liberec) and recorded by means of a recorder EZ 11 (Laboratorní přístroje, Prague).

The following parameters were used for measurements: the slit width of monochromator 0.04 mm, the voltage of photomultiplier 1.0 kV, the inlet resistance of MEK 100 amplifier

$10^7 \Omega$ and its sensitivity 300 mV, the sensitivity of recorder 5 mV and the chart speed 10 mm/min.

The decay of the emission of rubrene was measured at 555 nm and concentration $5 \times 10^{-6} \text{ mol l}^{-1}$ in carbon tetrachloride–chloroform mixture in a fluorescence cell of 1 cm width and 3 ml volume. During irradiation the solution was intensively stirred which ensured a homogeneous course of reaction in the whole volume. The concentration of oxygen in organic solvents was about $10^{-3} \text{ mol l}^{-1}$, that means by two orders of magnitude higher than the concentration of rubrene.

The stability of the source was checked by periodic measurements of the emission of a rhodamine B solution in ethylene glycol ($10^{-6} \text{ mol l}^{-1}$) in the wavelength region between 500 and 700 nm carried out under equal conditions as kinetic measurements. It was observed that the intensity of the source varied by about $\pm 5\%$ which did not affect measurements. Moreover, the photoperoxidation of rubrene without additions of an inhibitor was repeated several times during measurements.

Results

Quenching of triplet carbonyl groups

The quantum yield for the main chain scission is given by the formula

$$\varphi = \frac{c_p}{M_n(0)} \frac{s}{I_p t},$$

where c_p is the concentration of polymer in g l^{-1} , s is the number of the main chain scissions, $M_n(0)$ is the initial number-average molecular weight, I_p is the dose of radiation absorbed by polymer in einsteins per gram, and t is the time of irradiation.

The presence of a quencher affects the quantum yield. The ratio of quantum yields for the main chain scission without and with a quencher is given by following relationship

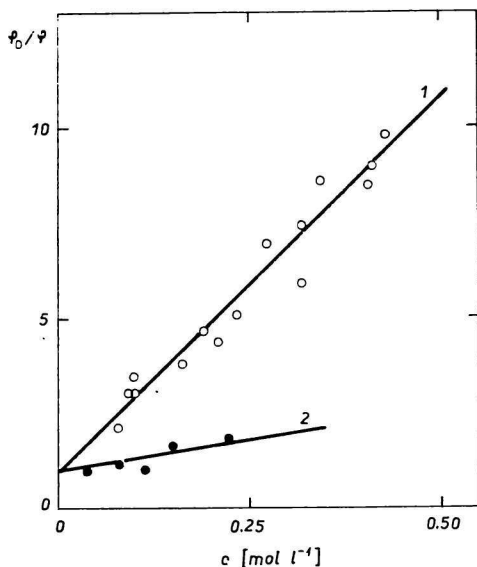


Fig. 1. Photolysis of poly(vinyl phenyl ketone) in film. 1. quenching by naphthalene; 2. quenching by nickel(II)(acac)₂.

$$\frac{\varphi_0}{\varphi} = \frac{s_0}{s} \frac{I_p}{I_p(0)},$$

where s and s_0 stand for the number of the main chain scissions with and without a quencher and I_p and $I_p(0)$ are the radiation absorbed by polymer in the presence and in the absence of a quencher respectively.

The number of main chain scissions may be determined from the decrease in molecular weight viscosimetrically according to equation

$$s = \left(\frac{[\eta]_0}{[\eta]} \right)^{1/\alpha} - 1,$$

where $[\eta]_0$ and $[\eta]$ are the limiting viscosity numbers of polymer before and after irradiation and α is the Mark-Houwink coefficient [9] which is equal to 0.84 for poly(vinyl phenyl ketone) in benzene at 30°C. The limiting viscosity number was calculated from the single-point measurements according to *Berlin* [33].

The ratio $I_p/I_p(0)$ is equal to one provided the quencher does not absorb at the wavelength of irradiation. If the quencher absorbs at this wavelength, the ratio $I_p(0)/I_p$ is given by the relationship

Table 2
Quenching efficiency

Compound	$\epsilon(366)$ [l mol ⁻¹ cm ⁻¹]	K_{SV} [l mol ⁻¹]	$K \cdot 10^3$ [l mol ⁻¹]	$k_q \cdot 10^8$ [l mol ⁻¹ s ⁻¹]
<i>p</i> -tert-Butylphenylsalicylate	0	0.0		
2-Hydroxy-4-methoxybenzophenone	1350	21.0		
2-Hydroxy-4- <i>n</i> -octyloxybenzophenone			0.01	0.0001
2-(2'-Hydroxy-5'-methylphenyl)benzo-triazole	8300	34.0		
2-(2'-Hydroxy-3'-chloro-5'-tert-butylphenyl)benzotriazole			0.01	0.0001
Nickel(II) <i>p</i> -tert-butylphenylsalicylate	560	1.6	8.50	0.15
Nickel(II) bis[2,2'-thiobis(4-tert-octyl)phenolate]	240	6.8	32.00	0.57
Nickel(II) <i>n</i> -butylamine-2,2'-thiobis-(4-tert-octyl)phenolate	240	0.0	61.00	1.08
Nickel(II) bis(butyl-3,5-di-tert-butyl-4-hydroxybenzyl)phosphate	3	3.0	5.2	0.090
Nickel(II) acetylacetonate	147	2.5	46.0	0.82
Cobalt(II) acetylacetonate	433	4.6 ^a	82.0	1.46
Zinc(II) acetylacetonate	0	1.0	6.1	0.108
Copper(II) acetylacetonate	535	0.0	2.1	0.037
Iron(III) acetylacetonate	2750	9.3 ^a	49.0	0.870
Chromium(III) acetylacetonate	640	15.0 ^a	0.3	0.005
Cobalt(III) acetylacetonate	880	15.0	520.0	9.20
Ferrocene	45	32.0	1.7	0.030
Naphthalene	0	18.3 ^{a,b}		
β -Carotene			3500.0	62.0

a) Average of two determinations.

b) In Ref. [9] the quoted value is 21.0 l mol⁻¹.

$$\frac{I_p(0)}{I_p} = \frac{1 - 10^{-D_p}}{D_p} \frac{D}{1 - 10^{-D}},$$

where D_p and D are the absorbances of polymer in film or in solution without or with addition of a quencher at the wavelength of irradiation (366 nm).

Dependence of φ_0/φ on the concentration of the quencher obeys the relationship

$$\varphi_0/\varphi = 1 + K_{SV} c,$$

where K_{SV} is the Stern–Volmer constant which is a measure of the quenching efficiency. The variation of φ_0/φ with the concentration of naphthalene and nickel(acac)₂ is shown in Fig. 1. The values of K_{SV} for the quenchers studied are listed in Table 2.

Quenching of singlet oxygen

The character of the decay of rubrene emission was different in the presence and in the absence of the quencher (Fig. 2) owing to photoperoxidation. From the initial slope of the kinetic curve we calculated the quenching constant K according to the following equation [22]

$$K = \frac{\frac{d([Ru]/dt)_0}{d([Ru]/dt)_0^Q} - 1}{[Q]},$$

where $d([Ru]/dt)_0$ and $d([Ru]/dt)_0^Q$ are the initial rates of decay in the absence and in the presence of quencher respectively, and $[Q]$ is the concentration of quencher.

The rate constant of bimolecular quenching of singlet oxygen equals [22]

$$k_q = (k_{ex}[Ru]_0 + k_d) K,$$

where k_{ox} is the rate constant for the reaction of rubrene with singlet oxygen (equal to $7 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$; [22]), k_d is the rate of the radiationless deactivation of singlet oxygen (equal to $0.143 \times 10^{-4} \text{ s}^{-1}$; [17]), and $[Ru]_0$ is the initial concentration (equal to $5 \times 10^{-6} \text{ mol l}^{-1}$).

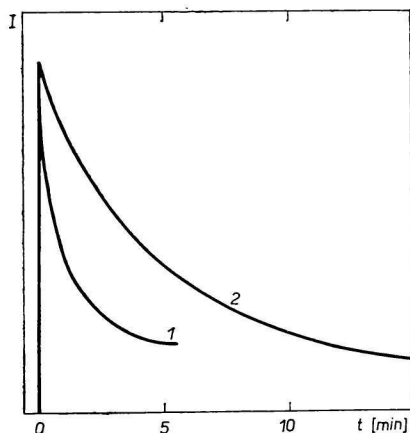


Fig. 2. Decrease in the fluorescence of rubrene (irradiation with $\lambda > 450 \text{ nm}$) as a function of time.

Concentration of rubrene $5 \times 10^{-6} \text{ mol l}^{-1}$, CCl_4 with 10 volume % of HCCl_3 , cell width 1 cm, volume of irradiated solution 3 ml; (I in arbitrary units).

1. In the absence of quencher; 2. in the presence of nickel(II)(acac)₂ ($10^{-3} \text{ mol l}^{-1}$).

The details concerning this record are given in Experimental.

Under these conditions the contribution of the term $K k_{\text{ox}}[\text{Ru}]_0$ to the total value of k_q is only 25%. Therefore it is important to know exactly k_d calculated from the reciprocal value of lifetime; it is sensitive to the composition of solvent. In order to dissolve the metal chelates we had to use an admixture of chloroform and therefore the value of the lifetime 700 μs is likely too high [17]. However, we have not succeeded in expressing quantitatively the reduction of the lifetime of singlet oxygen by the effect of a chloroform addition. Confrontation of the value found for the quenching by carotene in methylene chloride ($88 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ according to *Carlsson* [22] with the value $62 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ found in carbon tetrachloride demonstrates that the values obtained by the method described are correct.

Discussion

Confrontation of the values of the Stern—Volmer quenching constants K_{SV} with the rate constants of the bimolecular quenching of singlet oxygen (Table 2) leads to the following conclusions.

a) Besides their strong screening effect, the organic light stabilizers are quenchers of triplet carbonyl groups but very little effective quenchers of singlet oxygen.

b) Nickel(II) chelates are relatively little effective triplet quenchers but effective quenchers of singlet oxygen.

c) Acetylacetonates of bivalent and trivalent metals are effective quenchers of triplet carbonyl groups as well as singlet oxygen, their quenching power depending on the character of central atom.

It ensues from the measurements of the quenching of the triplet carbonyl groups of poly(vinyl phenyl ketone) in solution that the efficiency of quencher is given by its structure. It has been, however, demonstrated that the substituents do not influence the quenching provided a fundamental skeleton remains unchanged [34]. It is therefore surprising that great differences in the quenching efficiency were observed between the derivatives of 2-hydroxybenzophenone and 2-(2'-hydroxyphenyl)benzotriazole in polymer [7, 8] though a result consistent with our measurements was obtained with the model compounds in solution [23]. It is not possible to solve this inconsistency unambiguously on the basis of the measurements available. It will be necessary to perform further measurements of the quenching efficiency in polymer films under controlled conditions.

Nickel(II) chelates absorb poorly in the near ultraviolet region (280–400 nm) and, as our measurements show, they slightly quench triplet carbonyl groups. On the other hand, they quench singlet oxygen rather effectively in a model system. The value of this test consists only in a qualitative judgement whether a given substance is a quencher of singlet oxygen and in a relative estimation of its efficiency. This comparison is possible owing to the fact that singlet oxygen is independent of the way of its generation. The efficiency of the generation of singlet oxygen by the quenching of dialkyl carbonyl groups in polypropylene and its lifetime is another problem. For instance, *Carlsson* and *Wiles* [36] do not consider the macrocarbonyl chromophores to be the primary source of singlet oxygen. They are prone to assume that some aromatic hydrocarbons which come into nonpolar polymers from polluted atmosphere are initiators of singlet oxygen. The measurements of *Kearns et al.* [17] and *Adams* [18] demonstrate that singlet oxygen has a long lifetime in nonpolar solvents such as CCl_4 and CS_2 . Analogously a long lifetime may be assumed in the case of nonpolar polymers. Although we lack quantitative data to support these deductions, it may be assumed that singlet oxygen in nonpolar polypropylene may exist for a long time and thus play an important part in the photodegradation of this substance.

This conclusion concerns the photodegradation of polypropylene. In more polar polymers such as polyamides, polyethylene terephthalate, the singlet oxygen will exist for a much shorter time and the probability of bimolecular reaction must therefore be smaller. In the case of other polymers there may be another feature in the polymer structure that reduces the probability of a generation of singlet oxygen. From Table 2 it is obvious that β -carotene is a very effective quencher of singlet oxygen. In principle, β -carotene is a polyene. For this reason we may assume that the polyene structures in poly(vinyl chloride) can prevent the formation of singlet oxygen in this polymer.

It is obvious from Table 2 that the central atom as well as the ligand affect the quenching efficiency of metal chelates. The variation in the quenching efficiency caused by an exchange of ligand corresponds approximately to one order of magnitude while the exchange of central atom results in a variation of the efficiency by three orders. The most efficient chelate investigated in this study is cobalt(III)(acac)₃ and the least efficient is chromium(III)(acac)₃. On the other hand, their quenching efficiency with respect to triplet carbonyl groups is approximately equal.

These conspicuous changes in the quenching efficiency of singlet oxygen by metal chelates are certainly due to its convenient electron arrangement. It is not clear whether quenching is a physical process or chemical bonding of singlet oxygen into the coordination sphere of the complex. *Farmilo and Wilkinson* [37] consider the quenching of singlet oxygen by the nickel(II) complexes with 2-hydroxyacetoxime to be a physical process involving the energy transfer to the lowest triplet level the energy of which is lower than that of singlet oxygen. Provided this mechanism is also valid for other nickel(II) chelates investigated in this study, it is not clear why the energy transfer from the triplet carbonyl groups to this lowest triplet level of nickel(II) chelates does not take place. In the case of ferrocene it is supposed that the effect of heavy atom manifests itself in the quenching process [37].

The results of the investigations of the quenching of the carbonyl groups and singlet oxygen of nickel(II) bis{2,2'-thiobis[4-(1,1,3,3-tetramethylbutyl)phenolate]} provide a new insight into the interpretation of the results obtained by *Chien and Conner* [35] who compared the photooxidation of cumene initiated by *tert*-butyl peroxide and diethyl ketone. In this case a singlet energy transfer by the mechanism proposed by Förster cannot take place but the quenching of the singlet oxygen generated by the quenching of triplet carbonyl groups occurs.

The tests elaborated for the quenching of triplet carbonyl groups and singlet oxygen provide a deeper insight into the mechanism of efficiency of different types of light stabilizers. Since these tests are not time-consuming, they may be a guide for examining the new types of light stabilizers.

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