cate that at the higher temperature the chemisorbed species is capable of forming a stronger bond with the polymerization centers and thereby permanently deactiving them.

In comparing the GPC curves for polymer produced in both phases of the study, it appeared that the presence of oxygen resulted in a product of substantially higher molecular weight. This suggests that oxygen cannot function as a chain transfer agent and that the ratio of propagation to termination at active sites may increase as the number of sites is decreased. These molecular weight data, however, were not unambiguous since the effects of local overheating, which was clearly evidenced in some runs, made it difficult to determine what was truly representative of the intended reaction conditions.

The problem of local overheating arose primarily because the low sensitivity of the mass flowmeter necessitated relatively high rates of ethylene consumption, 500–1000 ml/min. By comparing these values (on a mass/volume/time basis) with consumption rates observed in previous studies[9] conducted at similar temperatures and pressures, it was determined that the present rates were not limited by the rate at which ethylene could dissolve in the diluent. As pointed out above, however, other mass transfer processes may have become significant during the later phases of those runs in which there was a large accumulation of polymer. Hence, concern is especially warranted in those instances when the product contained agglomerated or fused material.[30] Several recent papers[31-33] citing the importance of diffusion and heat transfer in Ziegler-type polymerizations tend to confirm the above concerns and to point up the need for more study of these phenomena in the supported chromium oxide polymerization system.

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(30) A reviewer has pointed out that in the slurry type polymerizations reported here the use of poorer solvents for polyethylene, such as *n*-hexane, is to be preferred.

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Quenching of Singlet Molecular Oxygen by Polyolefin Additives in Carbon Disulfide Solution

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ABSTRACT: Certain nickel chelates used in stabilizing polyolefins are highly efficient quenchers of singlet oxygen in carbon disulfide solution. The rate constants for quenching by bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II), [2,2′-thiobis(4-*tert*-octylphenolato)](*n*-butylamine)nickel(II), and (di-*n*-butyldithiocarbamate)nickel(II) are 5×10^8, 1.5×10^8, and 40×10^8 M^{-1} sec^{-1}, respectively; the rate constant for (di-*n*-butyldithiocarbamate)zinc(II) is 0.2×10^8 M^{-1} sec^{-1}. The $^1\Delta$ oxygen is produced by flash photolysis with conventional apparatus of oxygen-saturated carbon disulfide solutions containing Methylene Blue as sensitizer, and quenching rate constants determined by monitoring the disappearance of the acceptor, 1,3-diphenylisobenzofuran, at 435 nm.

A mechanism for the photodegradation of polyethylene has been proposed by Trozzolo and Winslow.[2a] One step in this mechanism involves the reaction of singlet oxygen ($^1\Delta$) with vinyl groups to form hydroperoxides. This proposal is supported by the detection of hydroperoxides at the surface of *cis*-polybutadiene after treatment with oxygen ($^1\Delta$).[2b] Hydroperoxide is also formed when singlet oxygen reacts with 1-docosene and *n*-tetracosane; in addition, there is evidence for attack at saturated carbon atoms in the polyethylene chain.[3]

If reaction of oxygen ($^1\Delta$) with polyolefins makes a significant contribution to their overall photodegradation, it should be possible to provide some protection by addition to the polymer of compounds which can efficiently quench singlet oxygen. This approach does not appear to have been intentionally adopted, but it is possible that some commercial polyolefin additives owe part of their effectiveness to their ability to quench singlet oxygen. To test whether this is a reasonable possibility, we have determined the effect of certain additives on the quenching of singlet oxygen in solution. The additives examined were the highly effective polyolefin stabilizers,[4] bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II), [2,2′-thiobis(4-*tert*-octylphenolato)](*n*-butylamine)nickel(II), and (di-*n*-butyldithiocarbamate)nickel(II); the zinc chelate, (di-*n*-butyldithiocarbamate)zinc(II) and the free ligand, 2,2′-thiobis(4-*tert*-octylphenol) were also examined.

Experimentally, it was convenient to study the influence of the chelates on the decay of singlet oxygen in carbon disulfide solution. A number of groups[5-9] have shown that the lifetimes of oxygen ($^1\Delta$) in various solvents can be measured by analysis of the disappearance of the acceptor, 1,3-diphenylisobenzofuran (DPBF). They used pulsed ruby lasers to excite a sensitizer such as Methylene Blue in air or oxygen-saturated solutions, and the singlet

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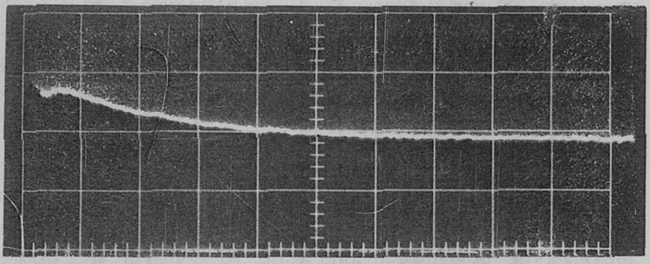

Figure 1. Typical decay curve for DPBF (initially 6.2×10^{-6} *M*) in oxygenated carbon disulfide: Methylene Blue concentration, 5×10^{-6} *M*; wavelength, 435 nm; transmission, 0–50% total range; time scale, 100 μsec/division.

oxygen was produced by energy transfer from the sensitizer. The lifetime of oxygen ($^1\Delta$) in carbon disulfide solution proved to be exceptionally long (~200 μsec), and it thus became possible to use a conventional flash photolysis apparatus for excitation of the sensitizer and production of singlet oxygen. The rate constants for quenching by the metal chelates were obtained from decay rates of DPBF in solutions containing metal chelates at concentrations of the order of 10^{-5} *M*.

Experimental Section

Materials. Methylene Blue and 1,3-diphenylisobenzofuran (Aldrich Chemical Co.) were used as supplied. 2,2′-Thiobis(4-*tert*-octylphenol), a gift from D. J. Carlsson, was recrystallized from cyclohexane, mp 135–136°. Bis[2,2′-thiobis(4-*tert*-octylphenolato)]-nickel(II) (from D. J. Carlsson) was recrystallized twice from ethanol. [2,2′-Thiobis(4-*tert*-octylphenolato)](*n*-butylamine)nickel(II) (Aldrich) was recrystallized from a chloroform–ethanol mixture and dried *in vacuo* at 55°. (Di-*n*-butyldithiocarbamate)nickel(II) (from D. J. Carlsson) was used as obtained. (Di-*n*-butyldithiocarbamate)zinc(II) (from D. J. Carlsson) was recrystallized from a chloroform–ethanol mixture, washed with ethanol, and dried *in vacuo* at 50°. Carbon disulfide (Fisher) was of Spectroanalyzed grade.

Procedure. The flash photolysis apparatus was of conventional design. The energy for the two xenon-filled flash tubes was supplied by a master and slave condenser bank (20 μF) charged to 4 kV. The flash duration under these conditions was approximately 35 μsec. Solutions of DPBF ($\lambda_{\max}$ ~430 nm) undergo some oxidation if exposed to the full output of the flash and it was necessary to cut off the radiation below 550 nm. This was achieved by interposing two layers of red photographic film (Diazochrome Red KRD Tecnifax) mounted on plate glass between the flash tubes and the photolysis cell. The plate glass was also taped to give a slit 3 mm wide for the light from the flash.

The bleaching of the DPBF was monitored at 435 nm. The IP21 photomultiplier tube was situated at the exit of a Heath EU-700 monochromator (slit setting, 150 μ) and the kinetic trace was recorded on a Tektronix 564B storage oscilloscope. The decay was followed for a total of 300–600 μsec. The change in percentage transmission varied from 7 to 18%.

Methylene Blue has a very low solubility in carbon disulfide and the solvent chosen for this study was carbon disulfide containing 2 vol % methanol. The solvent mixture was saturated with oxygen, and Methylene Blue was added to give a concentration of 5×10^{-6} *M*. The concentration of DPBF was 2.0×10^{-6} *M* for use in a cell of path length 15 cm and 6.2×10^{-6} *M* in a cell of path length 7 cm. DPBF solutions were prepared in a dimly lit room immediately prior to use. The metal chelates were added only minutes before the solutions were subjected to flash photolysis because some of them react slowly with Methylene Blue even in the absence of light.

Results and Discussion

Flash photolysis of oxygenated solutions of carbon disulfide, containing Methylene Blue as sensitizer and DPBF as acceptor, produces singlet oxygen in the $^1\Delta$ state; the $^1\Sigma$ oxygen produced simultaneously is thought not to affect these studies because of its short life in solution.[5] The

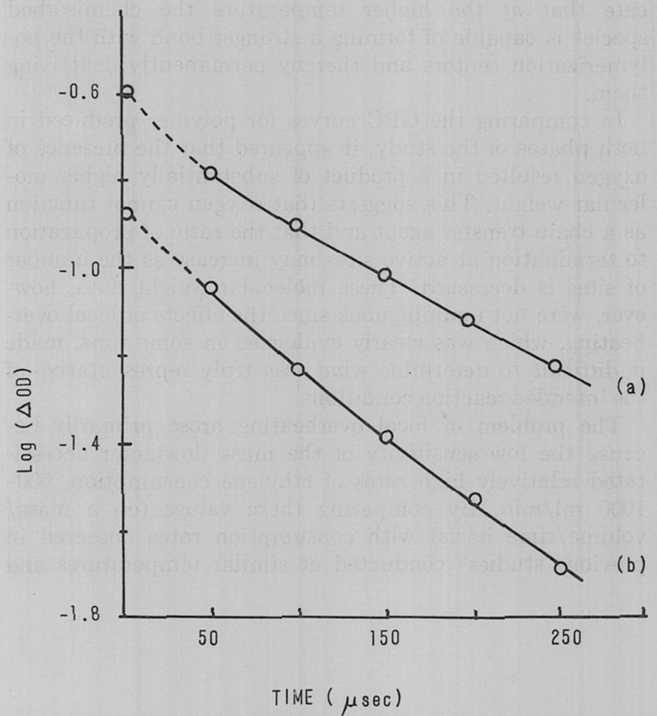

Figure 2. (a) Typical plot of log (ΔOD) *vs.* time in the absence of additive. (b) Plot of log (ΔOD) *vs.* time in the presence of 4.0×10^{-6} *M* bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II).

$^1\Delta$ oxygen can decay to the ground state by physical deactivation

$$^1\Delta \xrightarrow{1/\tau} {}^3\Sigma \tag{1}$$

with rate constant $1/\tau$, and it can react chemically with DPBF (A) to give a peroxide, AO_2

$$^1\Delta + A \xrightarrow{k_A} AO_2 \tag{2}$$

with rate constant k_A.[5] The decay of the oxygen ($^1\Delta$), monitored by means of the absorbance of DPBF at 435 nm, takes place over a period of about 600 μsec in carbon disulfide solution (Figure 1). If $[AO_2]$ and $[AO_2]_\infty$ are respectively the concentrations of AO_2 at time *t* and after all of the singlet oxygen has decayed

$$[AO_2]_\infty - [AO_2] = \frac{k_A[A][^1\Delta]_0}{1/\tau + k_A[A]} e^{-(1/\tau + k_A[A])t} \tag{3}$$

The change in concentration of DPBF is small and if [A] may be considered to be constant,

$$2.3 \log (\Delta OD) = -(1/\tau + k_A[A])t + \text{constant} \tag{4}$$

where Δ(OD) is the difference in optical densities at times *t* and ∞.

A typical plot of log (ΔOD) *vs.* time is shown in Figure 2a. The lifetime of the flash is about 35 μsec so that changes in ΔOD for times up to 50 μsec have little value. The slight deviation from linearity is ascribed to the change in [A] over the course of the measurements. Slopes taken at 100 μsec for two concentrations of DPBF yield values of τ and k_A of 250 ± 20 μsec and $(3.0 \pm 0.5) \times 10^8$ M^{-1} sec^{-1}, respectively, for the mixed-solvent carbon disulfide–methanol (98:2). Merkel and Kearns[5] quote values of 200 ± 60 μsec and ~3.5×10^8 M^{-1} sec^{-1} for τ and k_A in carbon disulfide–methanol (99:1). The results using standard flash photolysis equipment thus agree well with those obtained by means of the ruby laser pulse technique.

Quenching by Additives. Addition of a metal chelate,

Table I
Rate Constants for Quenching of Singlet Oxygen in Solution

	$k_Q \times 10^{-8}\ M^{-1}\ \mathrm{sec}^{-1}$		
Quencher	CS$_2$ (This Work)	Iso-octane[11]	Hexadecane[11]
Bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II)	5.0 ± 2.5	1.3, 2.0	1.3
[2,2′-Thiobis(4-*tert*-octylphenolato)](*n*-butylamine)nickel(II)	1.5 ± 0.8	1.8, 2.7	0.80
(Di-*n*-butyldithiocarbamate)nickel(II)	40 ± 15	70	9.0
(Di-*n*-butyldithiocarbamate)zinc(II)	0.2 ± 0.1		

Q, caused a more rapid decay of singlet oxygen as monitored by the disappearance of DPBF. The additional quenching is ascribed to

$$^1\Delta + \mathrm{Q} \xrightarrow{k_Q} {}^3\Sigma + \mathrm{Q}^* \quad (5)$$

and the rate constant for this process is k_Q. In the presence of Q, the dependence of peroxide concentration on time is given by

$$[\mathrm{AO_2}]_\infty - [\mathrm{AO_2}] = \frac{k_A[\mathrm{A}][^1\Delta]_0}{(1/\tau + k_A[\mathrm{A}] + k_Q[\mathrm{Q}])} e^{-(1/\tau + k_A[\mathrm{A}] + k_Q[\mathrm{Q}])t} \quad (6)$$

The variation of log (ΔOD) with time should follow the relationship

$$2.3 \log (\Delta \mathrm{OD}) = -(1/\tau + k_A[\mathrm{A}] + k_Q[\mathrm{Q}])t + \text{constant} \quad (7)$$

A plot of log (ΔOD) *vs.* time for a 4.0×10^{-6} *M* solution of bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II) is shown in Figure 2b. τ and k_A are known from measurements in the absence of additive and the value of k_Q can be obtained from the slope at 100 μsec. The results for the various metal chelates are summarized in Table I.

Experiments were also performed with the additive 2,2′-thiobis(4-*tert*-octylphenol) at concentrations up to 2×10^{-4} *M*. The slopes of the log (ΔOD) versus time plots were largely unaffected by the addition of the phenol, but the intercepts were substantially reduced. The results suggest that at relatively high concentrations, this additive can compete with oxygen in quenching the Methylene Blue triplets. There is no experimental evidence for quenching of Methylene Blue triplets by the metal chelates. Quenching by molecular oxygen proceeds at approximately one-ninth of the diffusion controlled rate.[10] The concentration of oxygen in an oxygen-saturated solution of carbon disulfide is about 7×10^{-3} *M* at 25° and the concentrations of the bis[2,2′-thiobis(4-*tert*-octylphenolato)]nickel(II), [2,2′-thiobis(4-*tert*-octylphenolato)](*n*-butylamine)nickel(II), (di-*n*-butyldithiocarbamate)nickel(II), and (di-*n*-butyldithiocarbamate)zinc(II) were respectively 4×10^{-6}, 1.6×10^{-5}, 1.0×10^{-6}, and 1.0×10^{-4} *M*. The additives are thus present at sufficiently low concentrations that, with the possible exception of the zinc chelate, they would contribute little to the quenching of the Methylene Blue triplets.

Table I also includes some of the results of Carlsson, Mendenhall, Suprunchuk, and Wiles[11] for the quenching of singlet oxygen by nickel chelates in the solvents isooctane and hexadecane. These authors produced their oxygen ($^1\Delta$): (a) by photolysis of rubrene solutions, (b) from triphenyl phosphite ozonide decomposition, (c) by a microwave discharge. The agreement between the results obtained under various conditions is fairly good and we may conclude that certain nickel chelates are efficient quenchers of singlet oxygen in hydrocarbon or carbon disulfide solutions. The quenching is probably a physical process because exposure of chelate solutions to singlet oxygen results in a negligible change in their uv spectra.

The results described here and by Carlsson *et al.*[11] show that nickel chelate additives are highly efficient quenchers of oxygen ($^1\Delta$) in carbon disulfide, isooctane, and hexadecane solutions. They do not prove that the chelate additives protect solid polyolefins to any extent through their ability to deactivate singlet oxygen. In a recent letter,[12] Carlsson, Suprunchuk, and Wiles have compared the quenching rate constants, k_Q, for a range of quenchers and stabilizers with the lifetime of polypropylene under carbon arc irradiation. They show that (diisopropyldithiocarbamate)nickel(II) has a high k_Q (3.4×10^9 l. mol^{-1} sec^{-1} in methylene chloride) and that it extends the lifetime of polypropylene from 110 to 1300 hr, while (diisopropyldithiocarbamate)zinc(II) has a low k_Q ($<0.1 \times 10^8$ l. mol^{-1} sec^{-1}) and extends the lifetime of polypropylene to only 186 hr. With many of the other stabilizers the correlation between k_Q and polymer lifetime is poor and this is taken as evidence that oxygen ($^1\Delta$) deactivation is only one of the mechanisms whereby additives stabilize polyolefins. Carlsson *et al.* have shown that nickel(II) chelates can prevent the oxidation of rubrene by a stream of singlet oxygen when the quencher and the rubrene are present as thin solid layers. We are presently exploring the extent to which metal chelates affect the formation of hydroperoxide in solid polyolefins[3] and rubber[2,13] on exposure to singlet oxygen.

Acknowledgments. We are grateful to Drs. Carlsson and Wiles, National Research Council of Canada, for considerable discussion on polyolefin photodegradation and for gifts of additives. This research was supported by grants from the National Research Council of Canada.

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