Triplet-State Quenching by Photostabilizers of Polyolefins

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Synopsis

Paramagnetic nickel(II) complexes which are used as commercial photostabilizers of polyolefins are shown in laser photolysis studies to quench the triplet state of benzophenone in dilute benzene solution.   The efficiency of quenching observed is less than that of diamagnetic square-planar nickel(II) complexes which are more effective photostabilizers of polypropylene in "Xenotest" experiments.   The observed rate constants for quenching of triplet benzophenone are compared with those observed by other workers for quenching of singlet oxygen, $O_2^*(^1\Delta_g)$, in dilute solution.   The relevance of these studies to the understanding of photodegradation in polyolefins is discussed.

INTRODUCTION

The four basic types of stabilizers which are generally employed to inhibit thermal and photochemical degradation of polyolefins are antioxidants, peroxide decomposers, ultraviolet screeners, and so-called "reactive photostabilizers."   The function of the antioxidants and peroxide decomposers in inhibiting and limiting the free-radical chain reactions responsible for polyolefin oxidation is fairly well understood, as is the role of ultraviolet screeners.   An inert ultraviolet screener is one which harmlessly dissipates as heat photo-absorbed energy which would otherwise be absorbed by carbonyl or peroxide groups in the polymer resulting in autocatalytic photo-oxidation of the polyolefin.   The mechanism of photostabilization by reactive stabilizers which may be various has been the subject of several recent investigations.[1-3]

It has been proposed by several workers that reactions of excited triplet states of carbonyls are of importance in the photodegradation of polyolefins and that the mechanism of stabilization by reactive stabilizers involves quenching of the excited states of the carbonyl compounds.   In the past, it has been impossible to study the triplet states of reactive carbonyl compounds directly in flash photolysis studies because of their rapid decay; but recent developments in laser photolysis have made such studies possible.[4,5]   The present paper examines the ability of several nickel complexes which are either used commercially or are analogues of those which

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are so used to quench the lowest electronically excited triplet state of benzo-phenone. Benzophenone was chosen for investigation since its triplet state is well characterized and a great deal is known about its properties.
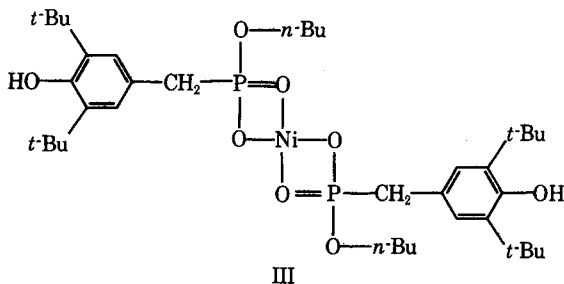
The structures of the nickel chelates used as potential quenchers are given below:
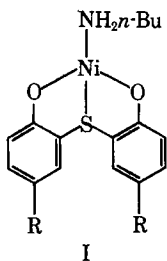
NH$_2$n-Bu
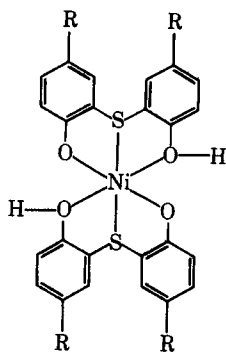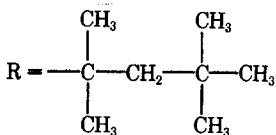
I

nickel(II) n-butylamine [2, 2'-thiobis(4-tert-octyl) phenolate]

R R

II

nickel(II) bis[2, 2'-thiobis(4-tert-octyl) phenolate]

$$R = -\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

III

nickel(II) bis(butyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphonate)

EXPERIMENTAL

The laser photolysis apparatus which has been fully described previously[5] utilizes a frequency-doubled Q-switched ruby laser which gives a ~20 ns pulse of ~25 mJ at 347 nm for excitation. Substantial absorption by triplet benzophenone at 535 nm was obtained from solutions of 10^{-2} mole l.$^{-1}$ benzophenone in benzene in a 1-cm^2 spectroscopic cell. The effect of various concentrations of the nickel complexes on the triplet decay was observed (see Fig. 1). Frequently the maximum concentration of quencher was limited by solubility or by its absorbance at the excitation wavelength (347 nm).

Benzophenone was B.D.H. laboratory grade which was recrystallized, and the nickel stabilizers were kindly supplied by Dr. D. J. Harper of I.C.I. Organics Division. May and Baker's pure crystallizable benzene
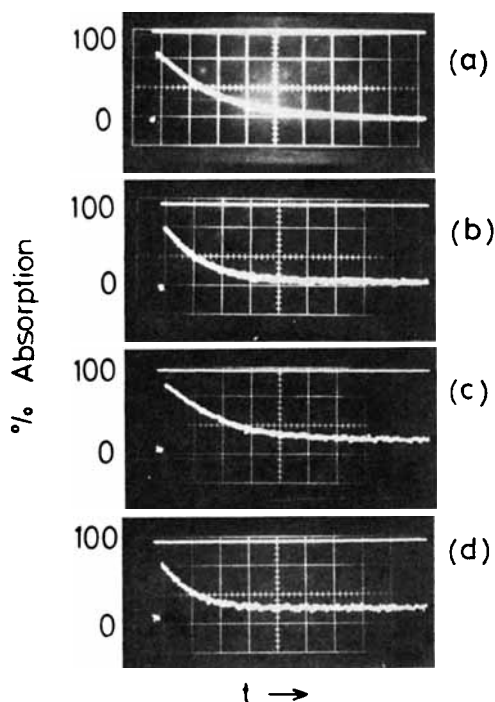
Fig. 1. Decay of triplet benzophenone absorption at 535 nm in the presence of (a) 0, (b) 1.0, (c) 2.0, and (d) 4.0 $\times$ 10^{-3} mole l.$^{-1}$ of nickel(II) bis(butyl-3,5-di-*tert*-butyl-4-hydroxybenzyl phosphonate) in deaerated benzene at 22°C. Time bases for (a) and (b), 1 μs per div.; (c) and (d), 0.5 μs per div.

was used throughout as solvent. Deaerated samples were obtained by several freeze, evacuate, and thaw cycles in the usual manner.

RESULTS

In benzene solution, triplet benzophenone decays by a pseudofirst-order process (see Fig. 2). The decay of triplet benzophenone can be represented as

$$\frac{-d[{}^3D^*]}{dt} = k_1[{}^3D^*] + k_{O_2}[O_2][{}^3D^*] + k_Q[Q][{}^3D^*] \tag{1}$$

where ${}^3D^*$ and Q represent the triplet state of benzophenone and the quencher, respectively, k_1 is the first-order rate constant for triplet decay, and k_{O_2} and k_Q are the quenching rate constants for oxygen and quencher, respectively. If the pseudofirst-order decay constant k is defined as

$$k = k_1 + k_{O_2}[O_2] + k_Q[Q] \tag{2}$$

it follows that for each quencher Q, plots of k versus $[Q]$ in the absence or presence of constant amounts of oxygen should give straight lines of slope k_Q (see Fig. 3).

Quencher	k_Q, 10^8 l.mole^{-1}s^{-1}	
	Triplet benzophenone	$O_2^*(^1\Delta_g)$[a]
Nickel(II) n-butylamine[2,2'-thiobis(4-tert-octyl) phenolate] (I)	5.3	2
Nickel(II) bis[2,2'-thiobis(4-tert-octyl) phenolate] (II)	11	1.6
2,2'-Thiobis(4-tert-octylphenol)	4.0	0
Nickel(II) bis(butyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphonate)(III)	4.1	0.12[b]

[a] Average of values obtained by two different methods in reference 15.
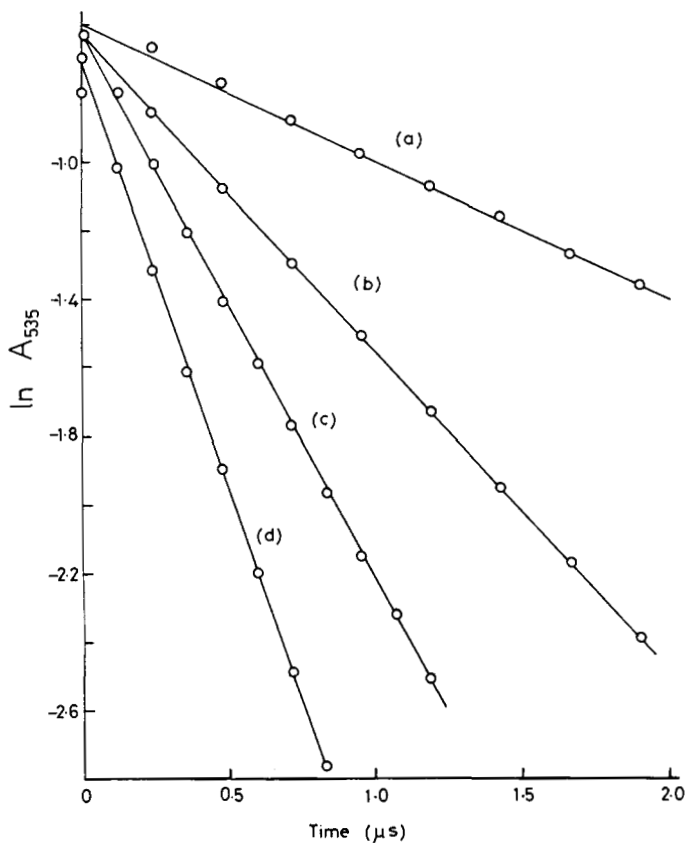[b] Solvent chloroform.

Fig. 2. First-order plots of decay of triplet benzophenone absorbance at 535 nm in the presence of (a) 0, (b) 1.0, (c) 2.0, and (d) 4.0 × 10^{-3} mole l.$^{-1}$ of nickel(II) bis-(butyl-3,5-di-tert-butyl-4-hydroxybenzyl phosphonate) in aerated benzene at 22°C.
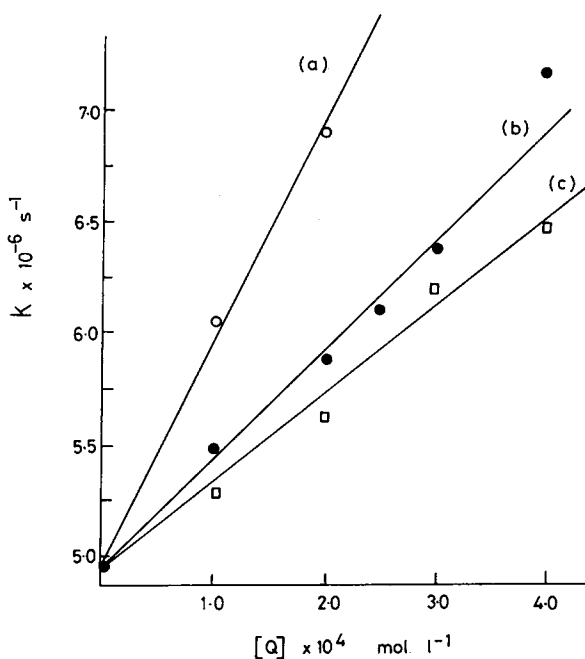
Fig. 3. Variation in the decay constant for triplet benzophenone as a function of quencher concentration, [Q], in aerated benzene at 22°C (a) nickel(II) bis[2,2'-thiobis(4-*tert*-octyl) phenolate], (b) nickel(II) *n*-butylamine[2,2'-thiobis(4-*tert*-octyl) phenolate], (c) nickel(II) bis(butyl-3,5-di-*tert*-butyl-4-hydroxybenzyl phosphonate).

None of the nickel complexes gave any observable transients when subjected to direct laser photolysis. Neither was any sensitized transient observed in the presence of oxygen. However, in the deaerated solutions of mixtures of benzophenone and the nickel complexes (I–III), long-lived transients were observed superimposed on the triplet benzophenone decay which showed quenching. The quenching constants obtained from analysis of the traces obtained from deaerated solutions agreed within experimental error with the values obtained from aerated solutions given in Table I.

Quenching of triplet benzophenone by 2,2'-thiobis(4-*tert*-octylphenol) was also observed in aerated solutions (see Fig. 4).

DISCUSSION

The three paramagnetic Ni(II) photostabilizers quench triplet benzophenone with rate constants which are an order of magnitude less than that which we reported recently for square planar diamagnetic Ni(II) complexes of certain salicylaldimines which also act as photostabilizers and almost certainly quench as a result of electronic energy transfer. The diamagnetic ligand 2',2'-thiobis(4-*tert*-octylphenol) quenches triplet benzophenone almost as effectively as compound I. This ligand did not, how-
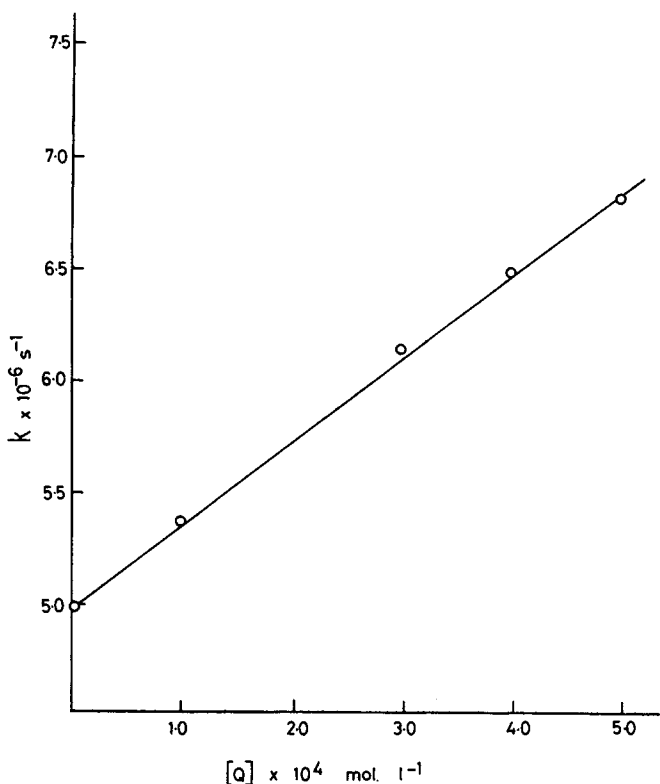
Fig. 4. Variation in the decay constant for triplet benzophonone as a function of [Q], the concentration of 2,2'-thiobis(4-*tert*-octyl) phenolate in benzene at 22°C.

ever, quench triplet phenanthrene or triplet 1,2-benzanthracene, which have lower energies than triplet benzophenone. Quenching by the ligand could either be due to electronic energy transfer to a triplet state of slightly higher energy than that of benzophenone or be due to hydrogen atom abstraction by triplet benzophenone. The small amounts of long-lived transient observed during the quenching experiments in deaerated solutions are consistent with the formation of the ketyl radical, $\phi_2\dot{C}$—OH (e.g., see ref 4).

The quenching constants obtained for these paramagnetic nickel(II) complexes are less than diffusion controlled. This has also been observed by previous workers for quenching of other triplet states by several paramagnetic metal complexes.[7-9] With paramagnetic quenchers of triplet states, both catalyzed intersystem crossing and electronic energy transfer are spin-allowed processes which for triplet quenchers may be represented as

1. $^3D^* + {}^3Q \rightarrow {}^1D + {}^3Q^*$ electronic energy transfer

and/or

2. $^3D^* + {}^3Q \rightarrow {}^1D + {}^3Q$ catalyzed intersystem crossing
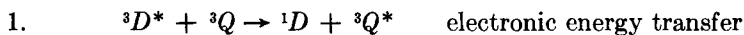
When the quencher has excited states of lower energy than that of $^3D^*$ and of suitable multiplicity reaction (1) is more likely than reaction (2) since catalyzed intersystem crossing involves the conversion of all the electronic energy of $^3D^*$ into vibrational energy which should be increasingly difficult for excited states of larger energy. In the case of triplet benzophenone, the energy to be dissipated amounts to ~290 kJ mole^{-1}, and other triplet carbonyls are likely to be similarly energetic. Several recent studies indicate that in a number of cases electronic energy transfer definitely occurs during quenching of triplet states by metal complexes[10,11] and that quenching is much less efficient when there is no possibility of electronic energy transfer.[12,13]

It seems likely, therefore, that the mechanism of the quenching of triplet benzophenone by the nickel photostabilizers is due to electronic energy transfer which is less than diffusion controlled because triplet ligand states lie at higher energies and because exchange interaction resulting in transfer to the lower-lying ligand-field states is sterically hindered.[6] In this case quenching by these photostabilizers of triplet carbonyls in polyolefins would be expected to be short range.

Briggs and McKellar[1] have reported a correlation between the quenching effect on triplet anthracene and the ability of diamagnetic nickel(II) complexes to stabilize photochemical degradation of polypropylene. A preliminary survey of the "Xenotest" of polystyrene containing these photostabilizers[14] shows some correlation with the ability to quench triplet benzophenone. For example, the highly efficient triplet benzophenone quenchers such as the square planar diamagnetic nickel(II) complexes were found to be the most effective UV stabilizers in these laboratory tests.[14]

Molecular oxygen is an ubiquitous paramagnetic molecule which quenches triplet-excited states very efficiently via electronic energy transfer, thereby being promoted to its lowest excited singlet state, $O_2^*(^1\Delta_g)$. This species is responsible for several photo-oxidations, and photodegradation of polyolefins might involve reaction of singlet oxygen formed during oxygen quenching of triplet carbonyls. Singlet oxygen, $O_2^*(^1\Delta_g)$, is quenched by nickel(II) photostabilizers,[15,16] and the rate constants for quenching of $O_2^*(^1\Delta_g)$ obtained by Carlsson and co-workers are given in Table I. The rate constant obtained in our laboratory for quenching of singlet oxygen by the diamagnetic nickel(II) bis(2-hydroxy-4-methylacetophenoxime) is 3×10^9 l. mole^{-1}s^{-1}. Once again the diamagnetic nickel(II) photostabilizers quench more effectively than the paramagnetic complexes in solution. Uri[17] considers that the fact that phenolic antioxidants are relatively inefficient as stabilizers argues against a "Bolland-Gee" free-radical mechanism[18] for the photodegradation. However, phenolic-type antioxidants are readily photo-oxidized,[19] and products arising from the depression of the Bolland-Gee mechanism can themselves be photosensitive (e.g., 4-peroxy-2,5-cyclohexadienones, aryl ketones, and quinones).[20,21]

Further studies are needed to elaborate the mechanism of photostabilization of nickel(II) complexes in polymers.[22] Obviously, a photostabilizer which can quench both reactive triplet states and any singlet oxygen formed

from those triplet states which are not quenched is likely to be doubly effective. It is hoped to extend these studies to polymer films where the relative quenching abilities of the various photostabilizers could well prove to be different from those found in solution, although the following paper[14] suggests that some correlation is likely.

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