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Photostabilizing Mechanisms of Hindered-Amine Light Stabilizers: Interaction with Electronically Excited Aliphatic Carbonyls[†]

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ABSTRACT: The quenching of n,π^* singlet and triplet states of acetone, a model compound for polyolefin ketone impurities, by hindered piperidines and hindered-amine light stabilizers (HALS) has been studied. Singlet-state quenching rate constants of piperidines are lower than the diffusional value and higher than the triplet-state quenching rate constants. The quenching efficiency depends on the steric hindrance at the nitrogen atom and on the ionization potential of the amine. Piperidine *N*-oxyl free radicals and hydroxylamino derivatives, compounds present in polyolefins stabilized with HALS and subjected to light exposure, are better quenchers than the parent piperidines. A comparison of the triplet quenching efficiency of the amines, and their derivatives, with that of *tert*-butyl hydroperoxide and di-*tert*-butyl peroxide allows the conclusion that the carbonyl-sensitized decomposition of the peroxide group is also efficiently quenched by HALS.

Introduction

Many studies on the photostabilizing activity of hindered-amine light stabilizers (HALS) for polymers have been published during the past decade.[1] Most of the published papers deal with the interaction between hindered amines and hydroperoxides or peroxides.[2-4] Hydroperoxides are formed as impurities of polyolefins primarily during the high-temperature conversion operations used in the manufacture of polymer artifacts.[5] In fact, hydroperoxides are the only chemical species unanimously recognized as an initiator of primary importance in the photooxidation of polyolefins.[5-9]

Ketone carbonyls are also believed to be important in the photodegradation of polyolefins. Their role in the initial stages of the photooxidation is much debated.[10,11] However, when the photooxidation goes on, the accumulation of carbonyl groups will cause an overwhelming concentration of the light absorption on the carbonyl chromophores. Chain scission would then occur via the classic Norrish I and II reactions of aliphatic ketones. Moreover, in a study on the photodegradation of an ethylene–propylene copolymer, Li and Guillet found a relatively efficient transfer of excitation energy from the keto group to hydroperoxides,[12] which subsequently decompose to give alkoxy radicals; alkoxy radicals undergo β-scission with decrease in molecular weight of the polymer. An interaction between the ketone group and hydroperoxides was also postulated to occur in an oxidized ethylene–propylene copolymer by Geuskens et al.[13,14] on the basis also of spectral evidence obtained for the system *tert*-butyl hydroperoxide–acetone.[15]

The effect of the addition of a commercial HALS, Tinuvin 770, on the phosphorescence of some carbonyl compounds has been studied in glassy solutions at 77 K.[16,17] Molecular motions are completely frozen in these conditions; this situation does not approach that of the polyolefins in the usual utilization conditions. In this study we examined the efficiency of some HALS and piperidines as quenchers of the excited states of acetone, a model compound of carbonyl impurities of polyolefins. The aim was to determine if the carbonyl excited-state quenching is an active path in the overall photostabilizing mechanism of HALS and how structural properties of these amines affect the quenching efficiency.

Experimental Section

Acetone was a Carlo Erba RP grade product. It was distilled over $KMnO_4$; the middle-cut fraction was collected. Piperidines were Aldrich products. When liquid, they were purified by distillation immediately before the preparation of the solutions; when solid, they were recrystallized from an appropriate solvent. 1,2,2,6,6-Pentamethylpiperidine and 4-hydroxy-1,2,2,6,6-pentamethylpiperidine were the same as synthesized for a previous work.[18] Piperidine *N*-oxyl free radicals were Aldrich products and were used as received. *tert*-Butyl hydroperoxide (80% in di-*tert*-butyl peroxide) and di-*tert*-butyl peroxide were Fluka products used as received. Commercial HALS Tinuvin 144, Tinuvin 622, and Tinuvin 770 were Ciba-Geigy products; Chimassorb 944 was a Chimosa product. A 12, A 31, and A 36 were Montefluos products; all were used as received. Their chemical formulas are reported in Chart I.

Techniques. Fluorescence quenching experiments were performed with a Perkin-Elmer MPF-44 fluorescence spectrophotofluorimeter by recording the frontal emission of air-equilibrated neat acetone, or solutions of the studied piperidine in acetone, contained in 1-cm path length quartz cells (λ_{exc} = 325 nm). The emission spectra were not corrected for instrumental response.

Phosphorescence lifetime measurements were carried out with laser photolysis equipment which uses a N_2 laser (Lambda Physik M 100 A, λ_{exc} = 337.1 nm, fwhm = 3.5 ns, peak power 1 MW) as exciting source. The light emitted after the laser pulse was detected at right angles with respect to the exciting beam. Given the feeble absorption of the 337.1-nm light of the laser by the solutions, particular attention was paid to the elimination of the scattered light of the laser. The light emitted was filtered with a cell, 2-cm path, containing chlorine and by a cutoff filter at 400 nm and then collected by a Bausch and Lomb high-intensity monochromator centered at 440 nm. The transient signals monitored by an RCA 1P28 phototube were stored by an R 7912 Tektronix transient digitizer. Data reduction and treatment were carried out by a standard computer program: the obtained curves fit a monoexponential decay. The solutions for phosphorescence

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Table I
Stern–Volmer Constants for the Quenching of Neat Acetone (K_{SV}) and 0.8 M *tert*-Butyl Hydroperoxide–Acetone Solution (K_{SV}') Fluorescence by Piperidines

compound	IP,[a] eV	K_{SV}, M^{-1}	$10^{-9} \times k_q$,[b] M^{-1} s^{-1}	K_{SV}', M^{-1}	K_{eq}[c] M^{-1}
piperidine (PIP)	8.7	2.5	1.5	1.6	1.0_2
2-CH$_3$-PIP	8.63	3.1	1.8_2	1.7	2.1
4-CH$_3$-PIP	8.61	3.0	1.7_5		
2,6-(CH$_3$)$_2$-PIP	8.53	2.9	1.7	1.5_5	1.5_8
2,2,6,6-(CH$_3$)$_4$-PIP	8.04	1.2	0.7_1	0.6_7	2.0
N-CH$_3$-PIP	8.37	3.1	1.8_2	1.8	1.1_5
4-OH-*N*-CH$_3$-PIP		2.0	1.0_6	1.1	1.9_2
2,2,6,6-(CH$_3$)$_4$-*N*-CH$_3$-PIP	7.68	2.2_5	1.3_2	1.7	0.3_6
4-OH-2,2,6,6-(CH$_3$)$_4$-*N*-CH$_3$-PIP		1.8	1.0_6		
2,2,6,6-(CH$_3$)$_4$-PIP *N*-oxyl		10.7	6.3	10.7	
4-OH-2,2,6,6-(CH$_3$)$_4$-PIP *N*-oxyl		9.5	5.6	9.5	
A 31		0.3_6	0.2_1		

[a] Ionization potentials taken from ref 47. [b] Calculated by taking τ = 1.7 ns as fluorescence lifetime of acetone (ref 24). [c] Thermodynamic equilibrium constant for the association reaction between piperidines and *tert*-butyl hydroperoxide.

Table II
Acetone Phosphorescence Quenching Rate Constants by Piperidines and Commercial HALS

compound	$10^{-8} \times k_q$, M^{-1} s^{-1}	compound	$10^{-8} \times k_q$, M^{-1} s^{-1}
piperidine (PIP)	1.6	*N*-OH-PIP	3.5
2-CH$_3$-PIP	2.1	2,2,6,6-(CH$_3$)$_4$-PIP *N*-oxyl	12.0
4-CH$_3$-PIP	2.1	4-OH-2,2,6,6-(CH$_3$)$_4$-PIP *N*-oxyl	15.1
2,6-(CH$_3$)$_2$-PIP	1.7	4-NH$_2$-2,2,6,6-(CH$_3$)$_4$-PIP *N*-oxyl	15.2
2,2,6,6-(CH$_3$)$_4$-PIP	0.3_8	Tinuvin 144	4.9
4-NH$_2$-2,2,6,6-(CH$_3$)$_4$-PIP	0.4_9	Tinuvin 622[a]	0.3_7
4-OH-2,2,6,6-(CH$_3$)$_4$-PIP	0.1_8	Tinuvin 770	0.2_1
N-CH$_3$-PIP	1.5	Chimassorb 944[a]	2.5
2-CH$_3$-*N*-CH$_3$-PIP	1.8	A 12	0.4
3-OH-*N*-CH$_3$-PIP	1.8	A 31	6.9
2,2,6,6-(CH$_3$)$_4$-*N*–CH$_3$-PIP	2.3	A 36[a,b]	3.6
4-OH-2,2,6,6-(CH$_3$)$_4$-*N*-CH$_3$-PIP	2.6		

[a] Calculated for the repeating unit. [b] Calculated in acetone/benzene (90/10 by volume) for solubility requirements of the compound.

lifetime determinations were degassed by five freeze–pump–thaw cycles at 10^{-5} Torr and sealed under vacuum.

All measurements were performed at room temperature (20 ± 2 °C). The values of k_q reported in Tables I and II are a mean of three independent runs whose reproducibility was ±5%.

Results and Discussion

Electronically excited aliphatic ketones are reactive in both singlet and triplet states; the reactivity in the two states depends on the molecular structure.[19,20]

Ketone groups are distributed at random along the chains of polyethylene, while methyl ketone groups, situated at the end of the chains, should prevail in polypropylene, as demonstrated by the study of Carlsson et al. on the photolysis products of oxidized polypropylene films.[21] Consequently, the choice of a low molecular weight aliphatic ketone, as a model for polyolefinic macroketones, is problematical.

Acetone was chosen because the chemical and physical properties of its singlet and triplet excited states are well-known;[22-25] moreover, it shows both fluorescence and phosphorescence emission in fluid solution at room temperature, which allows an easy study of its reactivity in the singlet and triplet states.

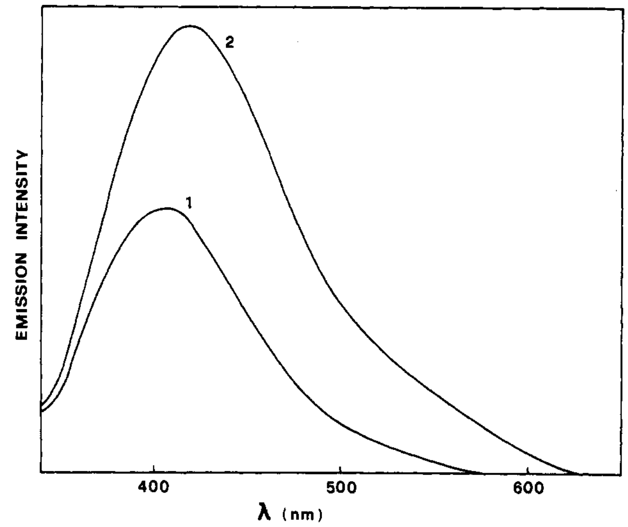


Figure 1. Emission spectra of neat acetone: (1) acetone air-equilibrated (fluorescence); (2) degassed acetone (fluorescence *plus* phosphorescence).

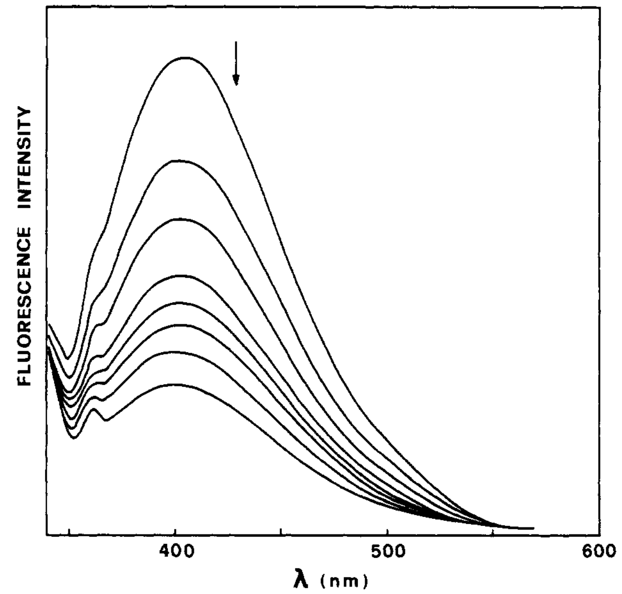
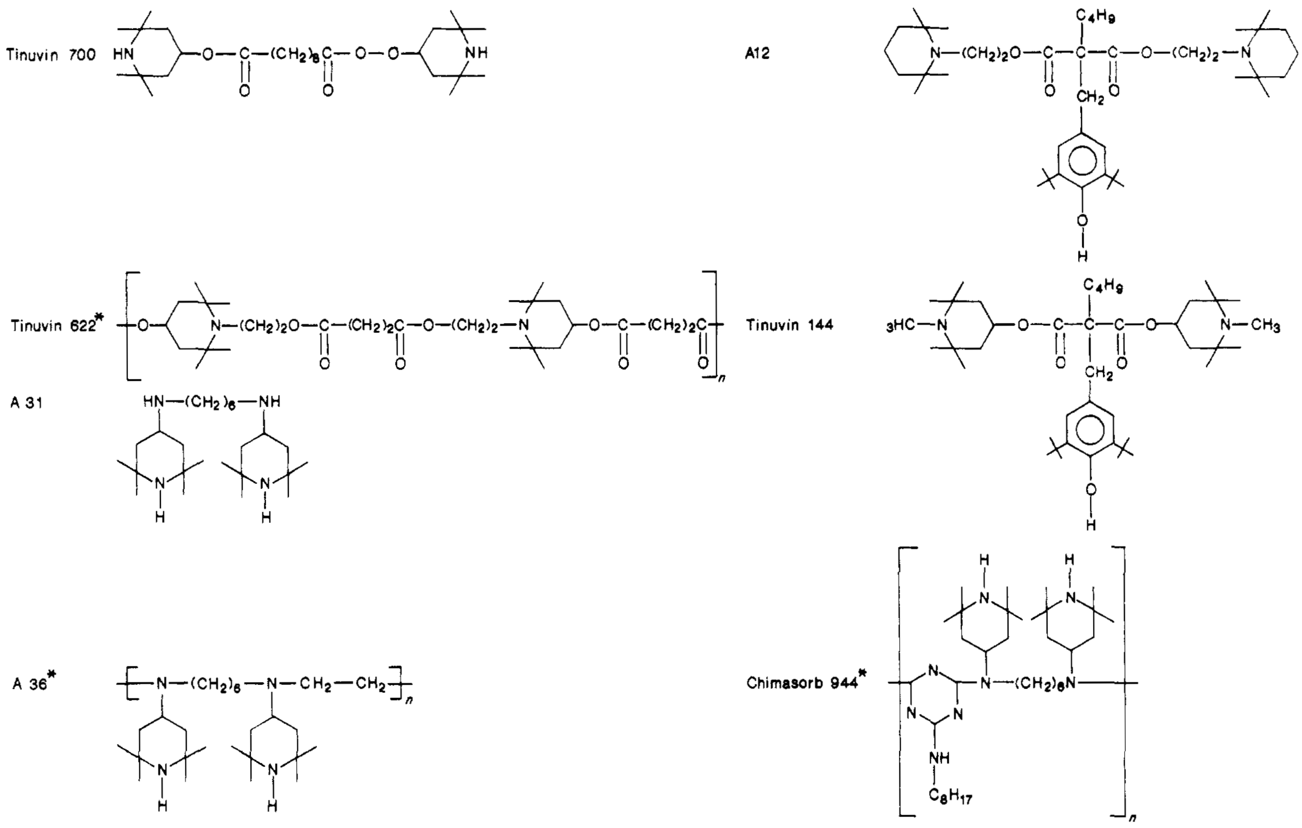


Figure 2. Quenching of acetone fluorescence by piperidine. [Piperidine] = 0, 0.1, 0.2, 0.33_5, 0.42, 0.5, 0.65, and 0.9 M.

Fluorescence Quenching Studies. The emission spectra of an air-equilibrated and a degassed cell of neat acetone are shown in Figure 1. The increase of the emission intensity and the shift in the maximum wave-

Chart I



length from 405 to 418–420 nm are associated with the appearance of the acetone phosphorescence in degassed medium.

Figure 2 shows the effect of the addition of piperidine to an air-equilibrated acetone cell. The decrease of fluorescence emission follows the linear Stern–Volmer relationship

$$\phi_0/\phi = 1 + k_q\tau_0[Q]$$

where ϕ_0 and ϕ are respectively the fluorescence quantum yields in the absence and in the presence of a concentration [Q] of piperidine, τ_0 is the lifetime of the excited singlet state of acetone in the absence of any quencher, and k_q is the fluorescence quenching constant. Table I collects the Stern–Volmer constants $K_{SV} = k_q\tau_0$ for the quenching of acetone fluorescence by some secondary and tertiary piperidine model compounds, two nitroxyl free radicals, and the oligomeric commercial HALS A 31. The quenching rate constants, k_q, calculated from the Stern–Volmer constants by taking the value of 1.7 ns for the fluorescence lifetime of neat acetone, as found by Halpern and Ware,[24] are also reported in Table I. The value of the diffusion constant, k_q, in the acetone for small molecules at 20 °C is 2×10^{10} M^{-1} s^{-1} (as calculated from the relationship $k_{diff} = 2 \times 10^5 T/\eta$, where $\eta = 0.003$ P is the viscosity of acetone at 20 °C).[26] This value represents the upper limit, in acetone, for processes that occur via a collisional mechanism. From an inspection of the values reported in Table I, it can be seen that both secondary and tertiary piperidines are good quenchers of the lowest excited singlet state of acetone ($k_q = 1.5 \times 10^9$ M^{-1} s^{-1}) and that an increase in the steric hindrance on the carbon atoms α to the piperidine nitrogen decreases the quenching efficiency. More efficient quenchers are the two piperidine *N*-oxyl free radicals examined, $k_q \simeq 6 \times 10^9$ M^{-1} s^{-1}; the values found are in agreement with the values earlier reported for the quenching rate constants of aromatic hydrocarbon singlet states.[27-29] The increase of the molecular size, which involves a reduced mobility of the molecule, is probably responsible for the low k_q value of A 31. k_q values for other commercial HALS available could not be obtained either because of an insufficient solubility of the compounds in acetone or because of an unfavorable light absorption characteristic of some molecules.

Ground-state interaction between acetone and *tert*-butyl hydroperoxide has been reported by Geuskens[15] on the basis of the UV absorption spectrum of a solution of the hydroperoxide in acetone. A 1.6 M acetone solution of *tert*-butyl hydroperoxide shows a $\simeq$15% decrease of the fluorescence emission, which is only partially due to a change in the light absorption by acetone, as revealed by the $\simeq$10% decrease of the emission in the presence of 1.6 M *tert*-butyl alcohol. The decrease of the fluorescence emission could be due to an interaction between carbonyl and hydroperoxide groups in the ground state (as proposed by Geuskens) or to an interaction between the n,π^* singlet excited state of the ketone and the hydroperoxide. In this latter case a decrease of the fluorescence lifetime should be observed. The attempts to determine variations in the fluorescence lifetime of acetone in the presence of *tert*-butyl hydroperoxide failed because of the resolution time of our fluorometer (about 1 ns), so no unequivocal interpretation of the nature of the interaction can be made by us.

It is widely accepted that the efficiency of hindered piperidines as stabilizers of polyolefins is associated with the following cyclic mechanism:[30]

$$>\text{N-H} \xrightarrow[\text{POO}^\bullet]{\text{-OOH}} >\text{N-O}^\bullet \quad (1)$$

$$>\text{N-O}^\bullet + \text{P}^\bullet \rightarrow >\text{N-O-P} \quad (2)$$

$$>\text{N-O-P} + \text{P-O-O}^\bullet \rightarrow >\text{N-O}^\bullet + \text{P-O-O-P} \quad (3)$$

Reaction 1 is favored by a local increase in piperidine

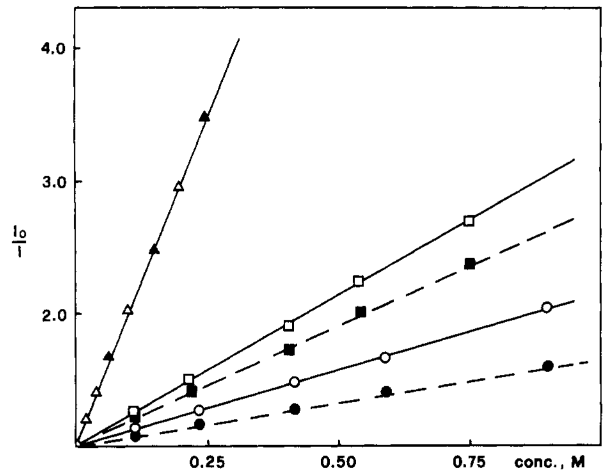


Figure 3. Stern–Volmer plots of acetone fluorescence quenching in the absence (open marks) and in the presence of 0.8 M *tert*-butyl hydroperoxide (closed marks): (○) 2,2,6,6-tetramethylpiperidine; (□) 2,2,6,6-tetramethyl-*N*-methylpiperidine; (△) 2,2,6,6-tetramethylpiperidine *N*-oxyl free radical.

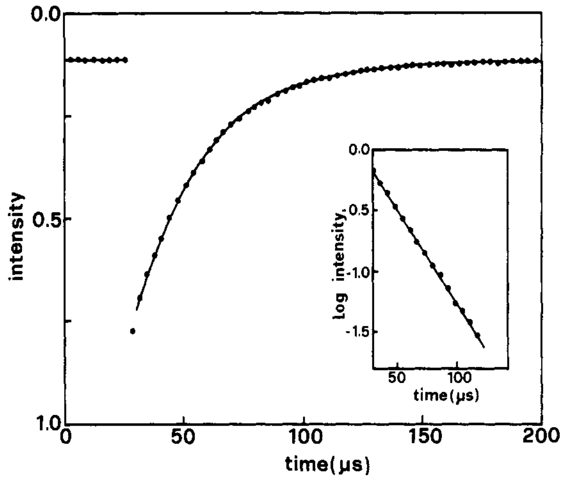


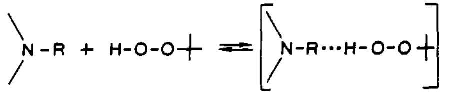
Figure 4. Transient emission, recorded at 440 nm, of a degassed neat acetone cell excited by a laser pulse at 337.1 nm. The insert shows the first-order decay of the emission.

concentration around hydroperoxide groups in the polymer; this increase is justified by the well-known phenomenon of association between amines and hydroperoxides.[31] In particular, association between *tert*-butyl hydroperoxide or cumyl hydroperoxide with 2,2,6,6-tetramethylpiperidine and some 4-substituted analogues has been demonstrated by Sedlar and co-workers.[32,33]

Moreover, nitroxide–hydroperoxide association, reported by Grattan et al.,[34] can raise the local NO• concentration in the regions of photounstable hydroperoxides where macroalkyl radicals can be formed by light absorption; this should favor reaction 2 with respect to the propagating reaction of alkyl radicals with oxygen:

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \xrightarrow{RH} ROOH + R^{\bullet}$$

We have attempted to obtain further information on the above-reported piperidine–hydroperoxide and piperidyl–nitroxide–hydroperoxide associations from fluorescence quenching studies. The quenching effect of piperidines on the fluorescence of an acetone solution containing *tert*-butyl hydroperoxide (0.8 mol/L) has been studied with the same experimental arrangement described for neat acetone fluorescence quenching studies. By addition of piperidines, a decrease of the fluorescence emission by acetone containing hydroperoxide was observed. As one can see from the results reported in Figure 3, a linear dependence of the ratio I_0/I on the amine concentration was observed; the slope of the plots obtained in the presence of *tert*-butyl hydroperoxide is lower than that obtained for neat acetone. K_{SV} obtained from the plots are reported in Table I. The low values of the Stern–Volmer constants obtained in the presence of *tert*-butyl hydroperoxide are easily explained if the following equilibrium is established:



With the reasonable hypothesis that only the free amine quenches the emission, a comparison of Stern–Volmer plots in the absence and in the presence of *tert*-butyl hydroperoxide allows the calculation of the concentration of the free amine and, hence, the value of the constant for the above equilibrium. The values obtained for some piperidines are collected in Table I. A comparison with the literature data (K_{eq} = 29 M^{-1} for 2,2,6,6-tetramethylpiperidine–*tert*-butyl hydroperoxide complex in cyclohexane)[32] shows that the K_{eq} obtained are about 1 order of magnitude lower. No evidence for association between NO• and *tert*-butyl hydroperoxide was obtained by this method: the Stern–Volmer plots in the presence and in the absence of *tert*-butyl hydroperoxide are superimposed. Probably, the reasons for these discrepancies with the literature reports are manifold. For piperidine *N*-oxyl derivatives the method is intrinsically unsuitable. These compounds are very efficient quenchers of the acetone fluorescence (as reported in Table I), so that relatively low concentrations are needed to obtain a good emission quenching; moreover, they are deeply colored (though the small absorption extinction coefficients in the region 360–420 nm allow an analysis of the acetone fluorescence to be made). This prevents the use of high quencher concentrations; otherwise deviations of the I_0/I plots from the linear should be observed due to absorption of the light emitted by acetone from the quencher itself. Therefore the analysis of the fluorescence quenching must be done with low *N*-oxyl concentrations and restricted to a concentration range too narrow to substantiate unequivocally the occurrence of the association with the hydroperoxide groups. Another source for the discrepancy is the self-association of hydroperoxides in solution.[35] The constant K_D for the equilibrium

$$2ROOH \rightleftarrows (ROOH)_2$$

has been reported to be 2.3 and 3.4 M^{-1} in carbon tetrachloride and cyclohexane, respectively,[32] when ROOH is *tert*-butyl hydroperoxide; no data are available for K_D in acetone. Even if it is reasonable to hypothesize that in the system acetone–hydroperoxide hydrogen-bonding phenomena[13] shift the equilibrium toward the monomeric form, in the absence of any quantitative data on the phenomenon, the values of K_{eq} reported in Table I have been calculated by neglecting the occurrence of the dimerization equilibrium of *tert*-butyl hydroperoxide and are, therefore, underestimated. However, it must be stressed that the fluorescence technique has confirmed the occurrence of association phenomena between hydroperoxide groups and hindered amines.

Phosphorescence Quenching Studies. Figure 4 reports the transient emission, monitored at 440 nm, from a degassed cell of neat acetone following excitation by a pulse of nitrogen laser; the emission follows a good first-

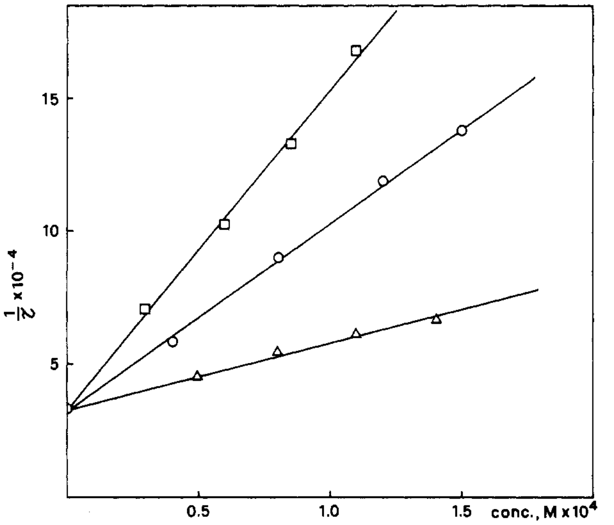


Figure 5. Neat acetone phosphorescence lifetimes as a function of quencher concentration: (△) Chimassorb 944; (○) A 31; (□) 2,2,6,6-tetramethylpiperidine *N*-oxyl free radical.

order decay law. The lifetime (τ_0) was found to be 30 ± 2 μs.

The phosphorescence lifetime of acetone in the presence of piperidine derivatives decreases. The simplest mechanistic scheme required to interpret the data is

$$\text{acetone } (S_0) \xrightarrow{h\nu} \text{acetone } (S_1) \xrightarrow{\text{isc}} \text{acetone } (T_1)$$

$$\text{acetone } (T_1) \xrightarrow{\tau_0} \text{acetone } (S_0)$$

$$\text{acetone } (T_1) + \text{Q} \xrightarrow{k_q} \text{products}$$

According to the above mechanism, the measured phosphorescence lifetime is given by

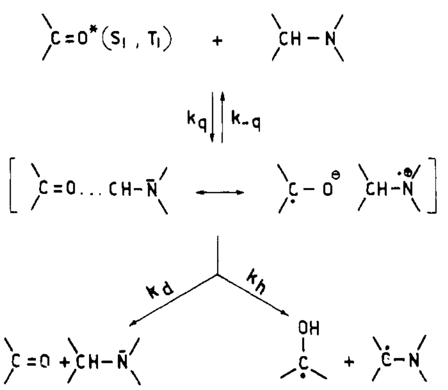
$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_q[\text{Q}]$$

From the above equation, a plot of $1/\tau$ vs. [Q] gives a straight line of slope equal to k_q and intercept equal to $1/\tau_0$. The results of the measurements of acetone phosphorescence lifetime in the presence of three different quenchers of the class of hindered piperidines are shown in Figure 5, in which $1/\tau$ is plotted as a function of the quencher concentration.

The values of k_q are summarized in Table II. These values, compared with those of the Table I, show that piperidines are better quenchers of the singlet than of the triplet state (the difference is about 1 order of magnitude); the same behavior is shown by piperidine *N*-oxyl free radicals, although the difference is less. The commercial HALS have quenching efficiency comparable to, and in some cases higher than, e.g., A 31 and TIN 144, those of the corresponding piperidine model compounds: the presence in all these compounds of more nitrogen atoms, which are believed to be mainly responsible for the quenching (see later), offers more statistical opportunities for the interaction with the excited carbonyl and counterbalances the reduced mobility of the molecule.

The large majority of the studies of the interaction of ketone excited states with amines deal with the reactions of aromatic ketones[36] and, hence, with the reactions of the triplet excited state. Only a few reports on the interaction of aliphatic carbonyl n,π^* singlet[25,37-39] and triplet[24,39-41] states and amines have appeared. The conclusions drawn from these studies are that for both aromatic and nonaromatic ketones the interaction between the amines and the ketone excited states (singlet or triplet) initially occurs through the formation of a charge-transfer complex in which the electrophilic half-vacant oxygen *n* orbital of the ketone is the electron acceptor and the amine lone pair is the electron donor. Then either hydrogen transfer and radical formation (k_h) or decay back to the ground state (k_d) occurs, as in Scheme I. The relative importance of k_h and k_d is related to the structure of the amine and of the carbonyl compound.[44] The above mechanism predicts that the quenching efficiency of the piperidines (as measured by k_q) toward an excited state of acetone is a function of the amine ionization potential (k_q increases with decreasing ionization potential of the amine) and of the ΔE_{0-0} of the excited state of the ketone itself (k_q increases with increasing ΔE_{0-0} of the excited state).[43-45] In agreement with the predictions, piperidines are better quenchers of the singlet (E_s = 84 kcal/mol) than of the triplet (E_t = 78 kcal/mol) state of acetone.[46] Ionization potentials for some of the examined piperidines are available,[47] and, in general, tertiary amines have ionization potentials lower than those of secondary amines.[48] An inspection of the k_q values reported in Tables I and II allows us to conclude that appreciable differences in quenching efficiency between secondary and tertiary amines are found only for hindered piperidines (compare the values for 2,2,6,6-tetramethylpiperidine and 1,2,2,6,6-pentamethylpiperidine). A similar behavior (lack of effect on going from secondary to tertiary amines) has been already found for the quenching of acetone fluorescence[38] and for pentan-3-one phosphorescence[36] by diethylamine and triethylamine and probably reflects the fact that the charge-transfer process is only a part, perhaps the most important one, of the overall quenching mechanism. In this respect, direct hydrogen atom transfer from *n*-hexylamine to triplet acetone was found in addition to complex formation.[25,39]

Scheme I



N-Hydroxypiperidine and piperidine *N*-oxyl free radicals are triplet quenchers more efficient than the corresponding piperidines. Their quenching mechanism, in particular that of *N*-oxyl free radicals, is not well understood: it seems that two mechanisms, at least, are operative.[49] Both substituted hydroxylamines and piperidine *N*-oxyl free radicals are present during the photooxidative degradation of polypropylene containing HALS, as revealed by Fourier transform infrared spectroscopy.[2] In irradiated polypropylene, the concentration of free piperidine groups steadily decreases with the irradiation time, while the concentration of substituted hydroxylamines increases and that of *N*-oxyl free radicals slowly declines after the initial rapid increase. So, the piperidines destroyed in the photooxidative process are replaced, with regard to their action as quenchers of carbonyl excited states, by compounds which are better quenchers than the starting amines.

On the basis of the results of a study on the photooxidation of polystyrene, Geuskens et al. in 1978 suggested that also for polyethylene and polypropylene the light energy, absorbed primarily by carbonyl groups, is transferred to hydroperoxide groups. The ensuing sensitized decomposition of hydroperoxides then becomes an important source of free radicals responsible for the oxidation.[50] This suggestion was corroborated by Li and Guillet, who reported that ethylene–propylene copolymers containing both keto and hydroperoxy groups have chain scission quantum yields much higher (0.2–1.3) than those containing only ketones (0.036). To explain these results, the authors proposed that the excited carbonyls form an exciplex with the ground-state hydroperoxides or peroxides in which the excitation energy, absorbed by the keto groups, is efficiently transferred to the hydroperoxidic groups.[51,52]

The recognized importance of the energy-transfer process from carbonyl excited states to peroxides and hydroperoxides makes interesting a comparison of the quenching ability of piperidines and the above-mentioned compounds. The triplet acetone quenching rate constants by *tert*-butyl hydroperoxide and di-*tert*-butyl peroxide as model compounds of the corresponding polypropylene macrogroups are 2×10^7 and 7.8×10^6 M^{-1} s^{-1}, respectively. In agreement with the literature data,[53-56] *tert*-butyl hydroperoxide is a better quencher than the corresponding peroxide; steric factors are believed to be responsible for this behavior.[54,55] The quenching rate constant of di-*tert*-butyl peroxide is in agreement with the values of ref 53 and 56, while k_q for hydroperoxy derivative is lower than those reported in ref 54 and 55. Possible reasons for this discrepancy can be the different molecular structure of the electronically excited donor (literature data are available for arylalkyl and aryl ketones) and ground-state hydrogen bonding between hydroperoxide and carbonyl groups.[14] Anyway, *tert*-butyl hydroperoxide is a quencher of the same efficiency (in the hypothesis that the k_q value we obtain is not heavily affected by the medium in which the experiments were carried out, neat acetone) or of lower efficiency than that of some HALS used as light stabilizers, but its quenching efficiency is certainly lower than that of piperidine *N*-oxyl free-radicals ($k_q \simeq 2 \times 10^9$ M^{-1} s^{-1}) and hydroxylamine derivatives ($k_q \simeq 4 \times 10^8$ M^{-1} s^{-1}), which are formed during the photooxidation of polyolefins stabilized with HALS. As HALS tend to migrate into regions rich in –OOH groups, one may conclude that the carbonyl-sensitized dissociation of hydroperoxidic groups is efficiently quenched by this class of photostabilizers.

Conclusions

Hindered piperidines and the products formed from their thermal or photochemical reactions with radical or molecular species present in polyolefins during the oxidative degradation efficiently deactivate the singlet and the triplet excited states of carbonyl keto groups. The classical Norrish I and II reactions occurring in the first $^3n,\pi^*$ state of ketones are efficiently quenched by piperidines and HALS. Moreover, the higher quenching efficiency of the above compounds toward the $^1n,\pi^*$ state make likely an abatement of the carbonyl reactions which come from the excited singlet state given, also, the fact that the "local" concentration of stabilizers can be much higher than the mean concentration. Finally, a comparison of the triplet quenching efficiency of *tert*-butyl peroxide and hydroperoxide with that of the piperidines and their transformation products leads to the conclusion that the dissociation of the peroxide bond, sensitized by intermolecular energy transfer from excited carbonyls, is also efficiently quenched.

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Registry No. PIP, 110-89-4; 2-CH_3-PIP, 109-05-7; 4-CH_3-PIP, 626-58-4; 2,6-$(CH_3)_2$-PIP, 504-03-0; 2,2,6,6-$(CH_3)_4$-PIP, 768-66-1; *N*-CH_3-PIP, 626-67-5; 4-OH-*N*-CH_3-PIP, 106-52-5; 2,2,6,6-$(CH_3)_4$-*N*-CH_3-PIP, 79-55-0; 4-OH-2,2,6,6-$(CH_3)_4$-*N*-CH_3-PIP, 2403-89-6; 2,2,6,6-$(CH_3)_4$-PIP *N*-oxyl, 2564-83-2; 4-OH-2,2,6,6-$(CH_3)_4$-PIP *N*-oxyl, 2226-96-2; 4-NH_2-2,2,6,6-$(CH_3)_4$-PIP, 36768-62-4; 4-OH-2,2,6,6-$(CH_3)_4$-PIP, 2403-88-5; 2-CH_3-*N*-CH_3-PIP, 671-36-3; 3-OH-*N*-CH_3-PIP, 3554-74-3; *N*-OH-PIP, 4801-58-5; 4-NH_2-2,2,6,6-$(CH_3)_4$-PIP *N*-oxyl, 14691-88-4; A 31, 61260-55-7; A 12, 75568-92-2; A 36, 88003-10-5; TINUVIN 144, 63843-89-0; TINUVIN 622, 70198-29-7; TINUVIN 770, 52829-07-9; CHIMASSORB 944, 71878-19-8; H_3CCOCH_3, 67-64-1; $(H_3C)_3CO_2H$, 75-91-2; $(H_3C)_3COOC(CH_3)_3$, 110-05-4.

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Characterization of Epoxy Cure by UV–Visible and Fluorescence Spectroscopy: Azochromophoric Labeling Approach

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ABSTRACT: Cure composition, reactivity ratio, activation energy, and weight-average molecular weight in two epoxy networks are investigated by an azochromophore labeling technique. The chromophore, *p,p'*-diaminoazobenzene (DAA), is used to mimic the reactivity of the curing agent, diaminodiphenyl sulfone (DDS). Reaction of DAA with epoxide produces red shifts, which have been deconvoluted on the basis of band assignments of model compounds. Thus, we obtain compositional analyses of cure products. Fluorescence due to the DAA label increases sharply due to the increasing fluorescence quantum yield of cure products containing tertiary amine rather than to viscosity changes. Fluorescence intensity has been used to estimate composition, based on kinetic differential equations, and these results have been compared with those obtained by UV–vis spectral deconvolution. Primary and secondary amines react at similar rates. The activation energy was estimated to be 16 kcal/mol on the basis of initial rate constants of the amine–epoxy reaction. Our experimental data were compared with the theoretically predicted weight-average molecular weight and soluble fractions. Finally, we compared UV–vis and IR techniques for the extent of cure in two epoxy systems. IR and thermal analyses suggest that DAA reacts a little faster than DDS. This difference in rates can be corrected by using a calibration curve.

Introduction

Recently, we reported a new method to obtain quantitative compositional information in the curing of epoxy with aromatic diamines by azochromophore labeling.[1] In this technique, we use a small amount of *p,p'*-diaminoazobenzene (DAA), which has reactivity similar to that of the curing agent diaminodiphenyl sulfone (DDS).[2] As the epoxy is cured, $\lambda_{\max}$ of the $\pi \rightarrow \pi^*$ transition corresponding to the azo bond of DAA is red-shifted in a way that provides spectral discrimination for the cure products (cross-linkers, branch points, linear chains, chain ends, and unreacted diamines).

The accuracy of our compositional analyses depends on the proper assignments of $\lambda_{\max}$ positions and the determination of the extinction coefficients for the various cure products. For this objective, we will first describe our attempt to make and separate model compounds by reacting DAA with a monoepoxy compound (glycidyl phenyl ether). We will use $\lambda_{\max}$ positions and extinction coefficients obtained from these model compounds in the deconvolution of the UV–vis spectra.

We have studied two epoxy networks in this work: DGEBA–DDS epoxy has a maximum T_g of 215 °C, which leads to a complete cure subject to degradation.[3] Furthermore, when this network is cured below 215 °C, vitrification occurs some time after gelation (e.g., 150 min at a cure temperature of 160 °C) according to its T–T–T diagram.[3] Since there is little progress in the cure reaction after vitrification, the extent of cure is also limited. Therefore, we chose another epoxy, DGEB–DDS epoxy (diglycidyl ether of butanediol–DDS), which has a maximum T_g of about 80 °C.[4] This epoxy when cured above 80 °C will gel but will not vitrify, thus pushing the cure extent almost to completion.

From these two epoxy networks cured at three isothermal temperatures, we have obtained a quantitative composition of each cure product covering a wide range of cure extents. With such experimental data, we first attempt to determine the reactivity ratio of the primary and secondary amines with the epoxy group. This ratio is predicted to have a strong effect on the cure process, including parameters such as gel time, molecular weight, and the elastically active network chains.[5-7] From the initial slopes of the rate constants of epoxy–primary amine reaction vs. the reciprocal temperature, we attempt to estimate the activation energy. Second, our data are compared under a certain assumption with the prediction of weight-average molecular weight as a function of cure by using Miller and Macosko's recursive theory for network.[7] Predicted soluble fractions are also compared with the composition of cure products.

We recently discovered that the total fluorescence intensity by the DAA label at 560 nm increases sharply as the cure proceeds.[9] This behavior is not due to the viscosity change, but rather to the increasing fluorescence by the cure products. The observed fluorescence intensities

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