

U.V. STABILIZATION OF POLYBUTADIENE*

STUART W. BEAVAN and DAVID PHILLIPS

*Department of Chemistry, University of Southampton, Southampton SO9 5NH
(Gt. Britain)*

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Summary

Following the recent interest in alternatives to u.v. protection of polymers by preferential absorption and in particular by methods depending on quenching of electronically excited states of chromophores present in these polymers, an investigation into the practicability of these quenching mechanisms in a commercial polybutadiene system has been undertaken. The mechanism of photooxidation for this polymer is reported and it is concluded that it is the quenching of the excited states of the α,β -unsaturated carbonyl compounds, formed in the auto-oxidative chain reaction, that must be achieved if stabilization by a mechanism of this sort is to be effective. Owing to the higher u.v. extinction coefficients of the α,β -unsaturated carbonyls formed in the polybutadiene system than of the saturated carbonyl chromophores formed in the photooxidation of polyolefin systems, it would also appear that the relative effectiveness of these quenching mechanisms favours its application in the former. Spectroscopic studies of testosterone, a model α,β -unsaturated ketone in poly(methyl methacrylate) matrices are reported, as are initial studies concerning the relative effectiveness of the various mechanisms to quench the excited singlet and triplet states of model carbonyls.

Introduction

The traditional approach to the problem of weathering and degradation of polymers induced by sunlight is the sensible one of the incorporation into the polymers of photochemically inert substances of high extinction coefficient which preferentially absorb the incident radiation, thus preventing absorption by chromophores present in the polymer which can lead to oxidative degradation, crosslinking and discoloration. The nature and mechanism of action of typical u.v. absorbers of this kind have been reviewed recently [1]. There has been much interest of late in alternative or supple-

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mentary methods of achieving u.v. stability which rely on the quenching of the electronically excited states of chromophores present in the polymers [2 - 10]. Such chromophores may arise from thermal processing, typically being carbonyl and hydroperoxide species, or may be impurities adventitiously present, or in some cases may form part of the polymer itself. Clearly, in order to probe the effectiveness of electronic quenching mechanisms in real polymer systems, as opposed to model systems, it is essential that the principal mechanisms of photooxidation be established, and the chromophores responsible for sensitizing degradation identified. Having elucidated a feasible mechanism, it is possible to investigate the quenching of electronically excited states of compounds which act as suitable models for the species responsible for photooxidation. Such studies should be carried out in the solid state, since the kinetics of bimolecular interaction in the solid differ greatly from those in the fluid state [11], but in general this condition has not been met. We report here some results on the mechanism of photooxidation of polybutadiene, and evidence that electronic quenching by additives used commercially may play a role in stabilizing the polymer. Some results on the quenching of model carbonyl compounds are also reported.

Results and discussion

Photooxidation of polybutadiene

There are several inter-related mechanisms principally responsible for photochemical weathering in hydrocarbon polymers. The most important feature is the classical chain autooxidation mechanism (Scheme 1).

Scheme 1:

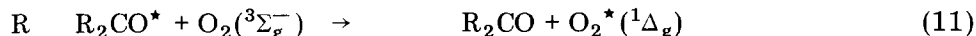
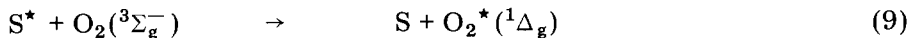


where RH represents the hydrocarbon polymer. Termination steps may involve any of the radicals present, and can lead to carbonyl production. Step (1) would typically involve the absorption of light by a carbonyl species followed by the homolytic production of free radicals by the Norrish type I mechanism (6), or absorption by a hydroperoxide to give alkoxy and hydroxyl radicals (7), both of which may initiate the sequence (2) - (5).

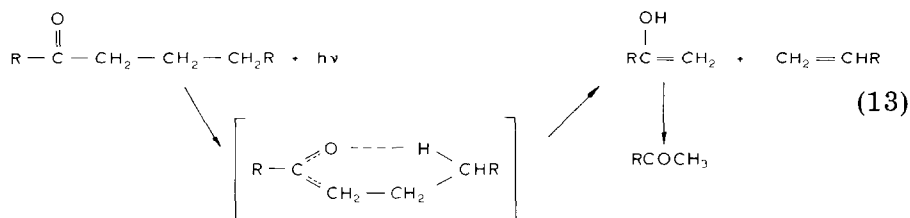


The hydroperoxides and carbonyl moieties responsible for the observed

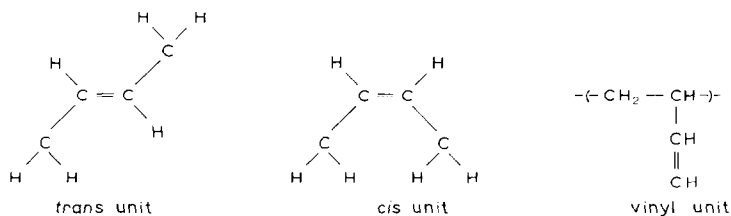
photoreactions will in general have arisen from prior thermal oxidation through sequences (2) - (5). Some hydroperoxide formation may well arise from reactions of $O_2(^1\Delta_g)$ which may be produced photochemically through adventitious sensitizers, (8), or from carbonyl sensitizers produced thermally (10).



Carbonyl species containing a γ -hydrogen may undergo photoreaction resulting in efficient chain scissions by the Norrish type II reaction:



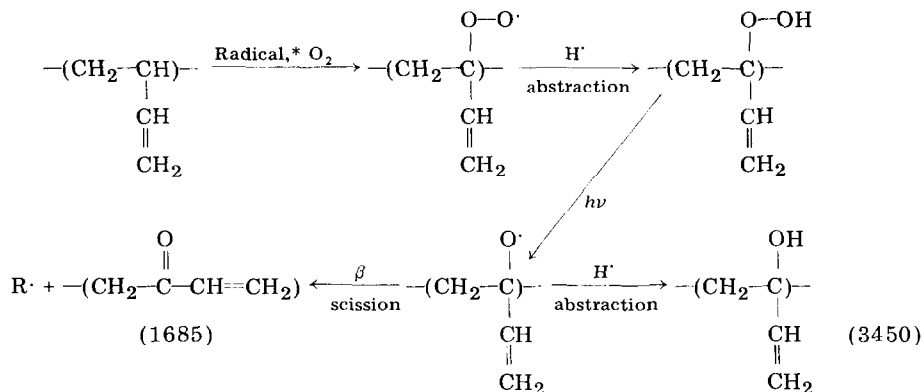
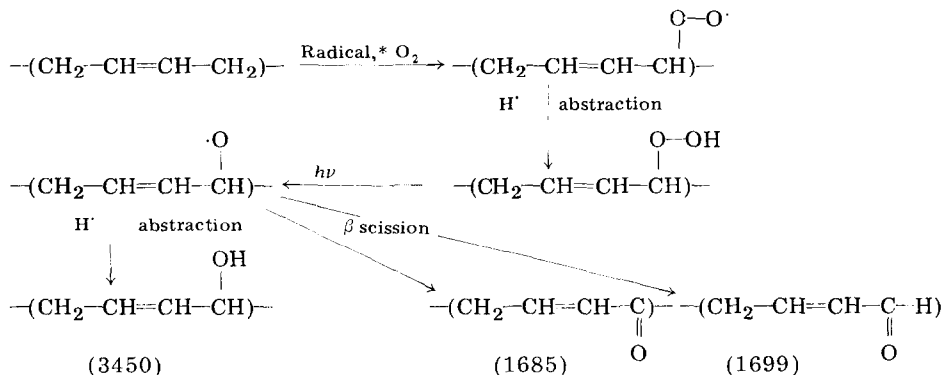
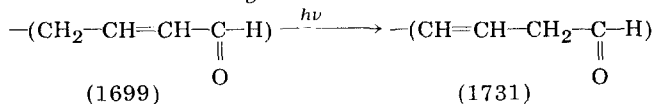
The exact nature of the degradation processes in any particular polymer is difficult to establish with certainty, but has been attempted in the case of the *secondary* oxidation of the commercial polybutadiene, Intene 45, which has the composition 48% *trans*, 42% *cis*, and 10% vinyl units.



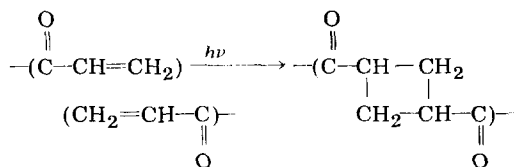
Full details of the experimental methods used, which included u.v., i.r., g.l.c. and mass spectral analysis, and detailed arguments in support of the mechanism have been given elsewhere [12] and will not be reproduced here. The scheme proposed to account for the major features in the photo and thermal degradation of this polymer are summarized in Scheme 2. It should be stressed that the scheme represents the secondary photolysis of the polymer, involving hydroperoxides and carbonyl compounds produced initially by thermal oxidation. Processes involving $O_2(^1\Delta_g)$ have been ignored but may play a role in hydroperoxide production. It is evident from the scheme that in addition to hydroperoxides which can initiate photooxidation, α,β -unsaturated aldehydes and ketones are also produced thermally which also undergo efficient photoreaction. Any attempts to stabilize the polymer

Scheme 2. Essential features of the photooxidation of polybutadiene

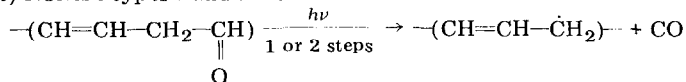
(a) Vinyl unit:

(b) *Cis*- and *trans*-1,4-units:(c) Subsequent photoreactions of α,β -unsaturated carbonyls:(i) loss of unsaturation *e.g.*

(ii) crosslinking



(iii) Norrish types I and II etc.



*Radical produced photochemically, *e.g.* from photodecomposition of hydroperoxides. Numbers in parentheses refer to frequency of i.r. band assigned.

against the effects of u.v. irradiation using electronic quenching mechanisms therefore must be directed towards the quenching of these species.

Quenching of electronically excited α,β -unsaturated carbonyls

It was found that upon both thermal and photooxidation of polybutadiene, the previously non-phosphorescent film became phosphorescent at liquid nitrogen temperatures. The phosphorescence and excitation spectra of thermally and photo oxidized film are shown in Fig. 1. Upon prolonged irradiation, the spectra of the thermally oxidized film grows into that of the photo-oxidized film, supporting the mechanism (Scheme 2) whereby α,β -unsaturated carbonyls ($\lambda_{em} = 520$ nm) are photoconverted to saturated carbonyls ($\lambda_{em} = 475$ nm). The possible mechanisms by which electronically excited α,β -unsaturated carbonyl compounds can be quenched are discussed fully below, but include triplet-triplet energy transfer. Making the reasonable assumption that the triplet states of α,β -unsaturated carbonyls might be involved in the photochemistry, we attempted to discover what role, if any, triplet-triplet energy transfer could play in the u.v. stabilization of polybutadiene by attempting to assess the triplet energy levels of twenty-six commercial u.v. stabilizers using phosphorescence methods. Clearly, for efficient energy transfer, the process has to be exothermic, and from the phosphorescence spectra shown in Fig. 1, the triplet energy level of the unsaturated carbonyl to be quenched can be assessed as $22,700 \pm 500$ cm⁻¹. A full account of these experiments has been given elsewhere [13] but a few of the important results are summarized in Table 1, and comparison made with those in a recent similar study [4]. In the present case, it is evident that only the two benzotriazole compounds have triplet energy levels low enough to be able to act as efficient acceptors of the α,β -unsaturated carbonyl donor energy. It is not perhaps mere coincidence that these two compounds prove to be the most efficient additives in commercial use. For the case of polystyrene photooxidation both the *o*-hydroxy benzophenone and benzotriazole type of additives should be efficient acceptors of the polystyrene carbonyl energy, and George [4] has shown that the efficiency of these additives is twice that expected on the basis of u.v. screening alone. In contrast, the efficiency of the nickel chelate compound Cyasorb U.V. 1084 compares favourably with that expected on the basis of screening [4], and this compound has too high a triplet energy level to permit efficient triplet energy transfer. In the case of polybutadiene oxidation, there is some further evidence that electronic energy transfer may be used successfully to deactivate excited α,β -unsaturated carbonyls. On introducing biacetyl (triplet energy 19,200 cm⁻¹) into the oxidized film, and illumination with light of wavelength 320 nm, at which wavelength biacetyl is practically transparent, the intensity of emission from the unsaturated carbonyl compounds is greatly reduced, and the characteristic phosphorescence of biacetyl is observed, indicative of triplet-triplet energy transfer. It is not suggested that biacetyl could be used commercially, but the experiment is a demonstration that the phenomenon does occur in real

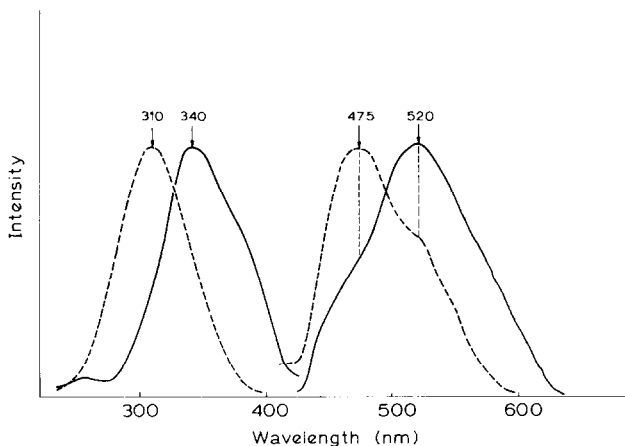


Fig. 1. Phosphorescence emission and excitation spectra of photo (---) and thermally (—) oxidized polybutadiene. Spectra uncorrected.

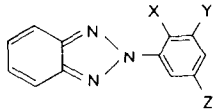
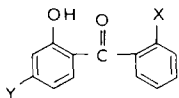
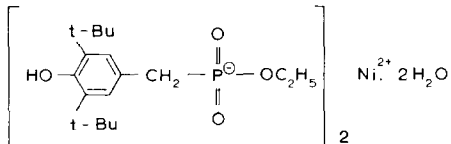
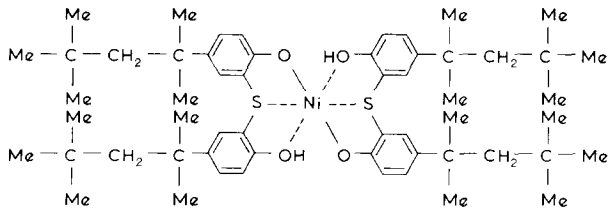
polymer systems, at least at low temperatures with modest concentrations of acceptor additive, despite recent predictions [3]. It should be stressed that it has yet to be proved whether or not the addition of triplet quenchers (other than the commercial benzotriazoles) to the polybutadiene system reduces the rate of photooxidation, but work is in hand to test this point.

Heller and Blattmann [3] have questioned whether or not quenching mechanisms can contribute towards u.v. stabilization, arguing that too high a concentration of acceptor is required before efficient triplet-triplet energy transfer occurs for such additives to be commercially viable. The argument is based upon a model with a fixed sensitizer with active site diameter of 5 Å, and a freely diffusing quencher of molecular weight 500. A plot is given which shows the quencher concentration necessary for quenching to occur within the lifetime τ of the sensitizer, and on this basis, it is shown that only additives with efficiency extending some 50 Å could be expected to deactivate efficiently at concentrations less than 0.5%. Since typical intermolecular distances for the exchange mechanism of energy transfer are of the order of up to 15 Å [11, 14], it would seem from the above arguments that the process should not be of importance. However, adopting a model of a rigid polymer, the average distance between donor and acceptor can be obtained from the equation [15]:

$$R_{av} = 0.55396 N^{-1/3} \quad (14)$$

For concentrations used typically in commercial practice in polybutadiene, say 10^{-1} M concentrations of additive, at least for the benzophenone-phenanthrene pair, the majority of donor molecules will have an acceptor molecule within a distance of 15 Å [16]. The extent of quenching is then determined by the lifetime of the donor molecule, since using the simple Perrin model [17], which is a good approximation for small acceptor concentrations [11], the quenching efficiency is given by:

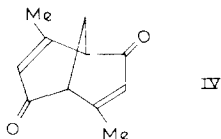
TABLE 1
Triplet energy levels of some commercial u.v. stabilizers

Commercial name	Structure		Triplet energy (cm ⁻¹)
Tinuvin P		X = OH Y = H Z = Me	22,000 ^a
Tinuvin 327	as above but with	X = OH Y = t-Bu Z = t-Bu	22,700 ^a <23,000 ^b
Cyasorb UV 9		X = H Y = OMe	23,800 ^b
Cyasorb UV 24	as above but with	X = OH Y = OMe	23,500 ^a
UV 531	as above but with	X = OH Y = OC ₈ H ₁₇	25,000 ^a
Irgastab 2002			24,700 ^a
Cyasorb UV 1084	2,2'-thiobis(4-t-octylphenylato) n-butylamine nickel		27,000 ^b
Ferro AM 101			26,900 ^a
Donor molecules:			
α,β-unsaturated carbonyl (polybutadiene degradation)			22,700 ± 500 ^a
polystyrene carbonyl			25,300 ^b
polypropylene carbonyl			29,500 ^b

^a This work. ^b ref. [4].

$$\frac{\Phi}{\Phi_0} = \exp(-C/C_0) \quad (15)$$

where C_0 is the concentration of additive at which quenching has the same rate as all other decay processes depleting the concentration of excited donor molecules. C_0 is thus dependent upon the donor lifetime. At low temperatures, where the triplet state donor lifetime is likely to be prolonged, there is abundant evidence that at the modest concentrations used commercially, triplet deactivation by exchange quenching processes is very efficient [14, 16]. We have demonstrated that under such conditions, the phosphorescence of a model α,β -unsaturated ketone (IV) is quenched by the additive Tinuvin P, giving rise to phosphorescence from the additive which clearly indicates triplet-triplet energy transfer (Fig. 2).



It has yet to be demonstrated that at ambient temperatures, where the triplet state donor lifetime will in general be short, triplet-triplet energy transfer will be an efficient deactivation route for a sensitizer at modest concentrations of additive. What is required is a thorough study of the process in the solid state over the temperature range from 77 K to ambient temperature, and such studies are currently being carried out in poly(methyl methacrylate) matrices.

There are some reasons to suppose that in the particular case of degradation of polybutadiene and its related copolymers quenching mechanisms may be effective, since the concentrations of additives used commercially are rather higher than in other polymers. The admittedly slender evidence that in this case and that of polystyrene degradation [4] those additives capable of triplet quenching appear to be the most effective is also an indication that the process may be of importance in particular cases. George [4] has stated that triplet-triplet transfer in polystyrene may be effective because it is known in this polymer that ketonic species play a major role in the degradation processes, unlike say in polypropylene in which hydroperoxide photodecomposition seems to be the major participating mechanism [18, 19]. Guillet [2] has shown that in the case of ketonic copolymers, triplet quenching by olefins (at relatively high concentrations) can effectively inhibit photochemical chain scission. In the present case the mechanism proposed to account for the degradation involves α,β -unsaturated carbonyls, and it is thus not perhaps unreasonable to expect that quenching may be of importance in this system.

The role of transition metal complexes, particularly those of nickel, as quenchers in polymer systems has been the subject of much discussion. It must be recognized that these additives may quench the singlet or triplet

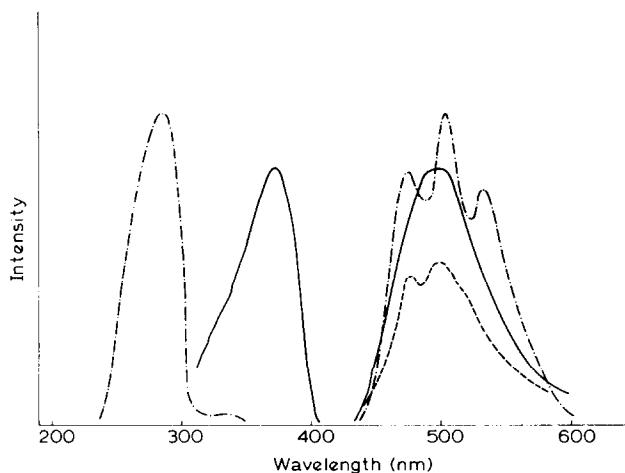
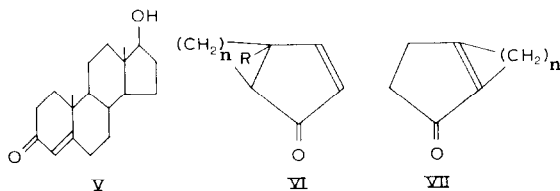


Fig. 2. (a) Phosphorescence excitation and emission spectra of Tinuvin P (- - - -); (b) phosphorescence excitation and emission spectra of (IV) (—); (c) total phosphorescence emission spectrum of Tinuvin P and compound (IV) mixture excited at 380 nm (- · - ·). All spectra uncorrected.

states of sensitizers present in processed polymers, or may quench $O_2(^1\Delta_g)$ which may be formed, and in addition, can act as u.v. absorbers. George [4] concludes that the efficiency of Cyasorb UV 1084 (Table 1), which clearly cannot quench by triplet energy transfer those ketonic species formed in polystyrene oxidation, is in fact exactly what would be expected on the basis of its u.v. absorption profile alone. Other workers, using a variety of nickel chelates and the polystyrene [7,8] system have shown a correlation between triplet quenching efficiency in solution and effectiveness of u.v. stabilization of the additives. In particular it was noted that the diamagnetic chelates were most effective, showing that quenching by enhancement of non-radiative decay is probably not of importance here. A correlation could equally well be drawn, however, between ability of the additives to quench $O_2(^1\Delta_g)$ and their effectiveness as stabilizers in the case of polystyrene and model compounds [6 - 8] and also in the case of simple alkanones [6, 19] which are models for ketonic species formed in polyolefin degradation. The direct quenching of the excited states of 2,6-dimethyl-4-heptanone [19] and 2-pentanone [9], and 4-methyl-2-pentanone [6] is found to be considerably less than diffusion controlled, in contrast to one report which claims that quenching of diethyl ketone sensitized photodecomposition of cumene by nickel chelates is diffusion controlled [10]. The weight of evidence appears to support the contention that direct quenching of triplet states involved in the photooxidation of simple polyolefins by any mechanism, including triplet-triplet energy transfer and enhancement of non-radiative decay, is not of importance as far as the nickel chelate additives are concerned.

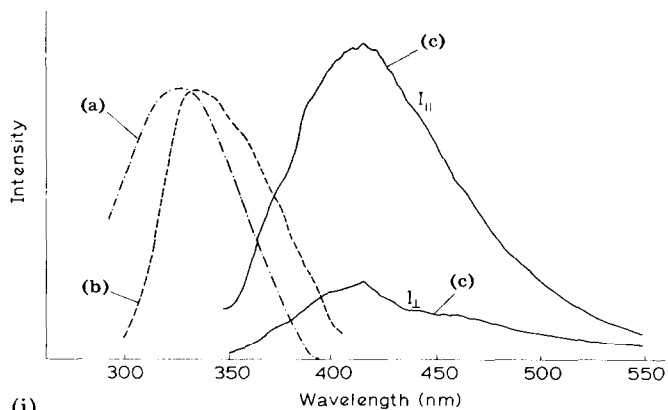
Model compound studies

We have developed the argument above that in the specific cases of some polymers, and in particular polybutadiene, electronic quenching of excited states may be a contributory factor in achieving stability of the polymers to exposure to u.v. radiation. If the efficiency of quenching is to be maximized, it is desirable to use additives which are known in the fluid phase to quench with unit or high efficiency the excited states of compounds which serve as models for chromophores known to be involved in photo-degradation in polymers. In the case of polybutadiene degradation, these are α,β -unsaturated carbonyl compounds, and one model compound, IV, has already been mentioned. Ideally model compounds should be both fluorescent and phosphorescent so that singlet and triplet quenching parameters can be evaluated. We have recently investigated testosterone (V) as a suitable model compound for the α,β -unsaturated carbonyls formed in polybutadiene degradation. In poly(methyl methacrylate) (PMMA) matrices at ambient temperature the compound has been shown to be fluorescent and at lower temperatures, is both fluorescent and phosphorescent (Fig. 3). In fluid media, however, the compound is non-luminescent. Testosterone clearly lends itself to quenching studies on both singlet and triplet states in the solid state, and these time-consuming quenching experiments are currently being carried out. The spectroscopy of the excited states is of some interest. The polarization of the fluorescence measured by a method previously described [15] shown in Fig. 4, clearly indicates a parallel transition since it is close to the theoretical maximum of +0.5 [20], and undoubtedly arises from the initially populated $^1n\pi^*$ state, which has a measured fluorescence decay time in the PMMA matrix at room temperature of 12 ns. The phosphorescence has a smaller positive polarization and shows evidence of structure, and the origin of the state is not clear. It has been shown that unsubstituted α,β -unsaturated ketones of the type (VI) have lowest triplet states of $n\pi^*$ character, with phosphorescence lifetimes typically of the order of 1 ms [21]. Disubstituted α,β -unsaturated of type (VII) have lowest triplet states of $\pi\pi^*$ character and typical lifetimes of the order of 100 ms [21].

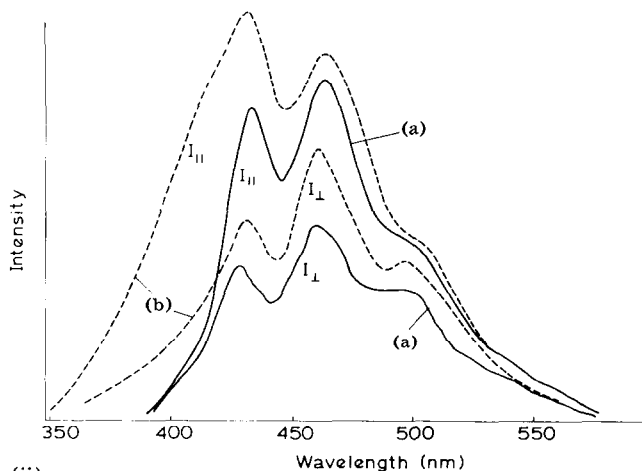


In the present case, the triplet lifetime is 11 ms, indicating intermediate character as might be expected from a monosubstituted α,β -unsaturated ketone. The relevant data are summarized in Fig. 5, and comparison made with data from another source [22].

In addition to studies being carried out on the α,β -unsaturated ketones, an investigation of the quenching in the fluid phase of the singlet state of a simple aliphatic ketone, 2-pentanone, by a variety of additives is being carried



(i)



(ii)

Fig. 3(i). (a) U.v. absorption spectrum of testosterone in methyl methacrylate monomer 298 K (---); (b) uncorrected fluorescence excitation spectrum of testosterone in poly(methyl methacrylate) at 298 K, emission monitored at 420 nm (---); (c) uncorrected fluorescence emission spectrum of testosterone in poly(methyl methacrylate) at 278 K, excitation at 330 nm. $I_{||}$ refers to the component of emitted light in the same plane as the vertically polarized exciting light and I_{\perp} to the component of emitted light in a plane at right angles to the vertically polarized exciting light. There has been no correction for the inherent polarization of the instrument.

Fig. 3(ii). (a) Phosphorescence spectrum of testosterone in poly(methyl methacrylate) at 77 K, excitation at 330 nm (—). (b) Total emission (phosphorescence and fluorescence) spectrum of testosterone in poly(methyl methacrylate) at 77 K, excitation at 330 nm (---). $I_{||}$ and I_{\perp} are as in Fig. 3(i). All spectra uncorrected.

out, in the hope of determining the relative efficiencies of different kinds of quenchers on such ketones. Quenching interactions include: (a) electronic energy transfer; (b) enhancement of non-radiative decay; (c) chemical reaction, (d) complex formation. (d) may in fact precede (a), (b) and (c) in many cases, to give an encounter complex in which stabilization may be

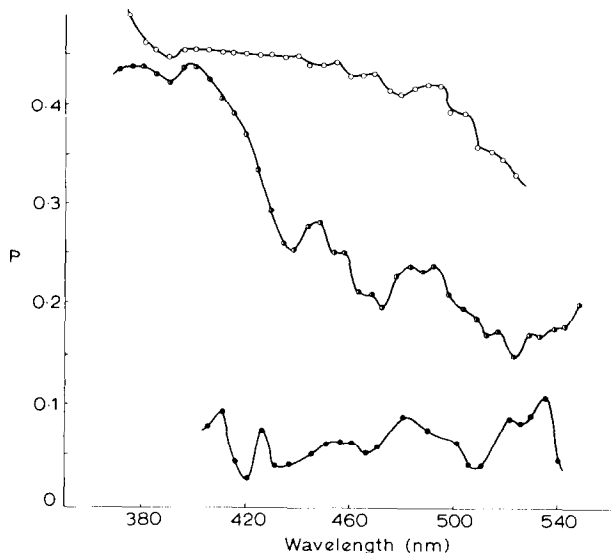


Fig. 4. Corrected polarization ratio P of (a) testosterone fluorescence at 298 K; (b) total emission of testosterone at 77 K; (c) testosterone phosphorescence at 77 K.

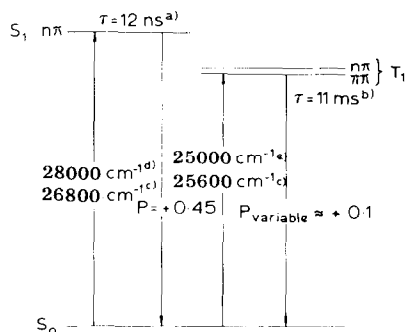


Fig. 5. Summary of testosterone luminescence data: (a) obtained by single photon counting with testosterone at 298 K in poly(methyl methacrylate); (b) obtained by monitoring phosphorescence decay with testosterone in methylcyclohexane at 77 K; (c) see ref. [22]; (d) obtained from onset of fluorescence; (e) obtained from onset of phosphorescence.

achieved by charge-transfer. Stern–Volmer plots for the quenching of the fluorescence of this ketone by a variety of additives, are given in Fig. 6, and rate constant data are tabulated in Table 2 and compared with similar data from the literature, with the likely quenching mechanism shown in each case.

Quenching by the electronic energy transfer mechanism is the most efficient for the series of quenchers listed, the quenching rate constants for singlet electronic energy transfer to the diketone and nickel chelate compounds being diffusion controlled [23] or better in the case of 2-pentanone and 2-butanone. Some of the quenchers whose effectiveness depends on

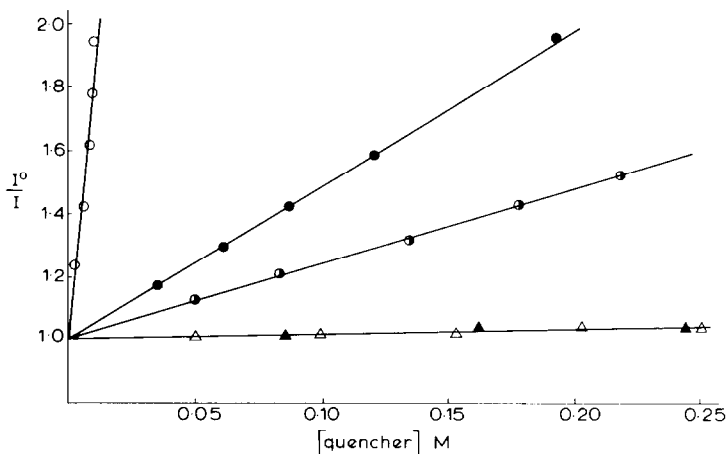


Fig. 6. Stern-Volmer plots for quenching of 2-pentanone fluorescence (9.39×10^{-3} M in cyclohexane) by: ○, biacetyl; ●, diethylamine; ○, triethylamine; ▲, carbon tetrachloride; △, 1-bromo-hexane.

charge transfer interaction followed by chemical reaction, *e.g.* the substituted ethylenes, have a moderate efficiency but in general this mechanism results in low efficiency quenching. If charge transfer is the rate determining step in the reactions of the two amine quenchers listed, then it would be expected that the amine with the lower ionization potential would have the greater quenching efficiency. As mentioned by Heller and Blattmann, however, it appears that ionization potential is not the only factor affecting the quenching efficiency of amines. Thus the ionization potential is lower for triethylamine than for diethylamine and yet the quenching rate constants for the former compound is less than the latter. The increase in steric hindrance in going from the secondary to tertiary amine could account for this. As to be expected from the high intersystem crossing yields of these aliphatic ketones, enhancement of non-radiative decay (1-bromo-hexane) results in very inefficient quenching of the first excited singlet.

A more comprehensive investigation of the quenching of a variety of model ketones by all of the mechanisms discussed briefly above is currently under way.

Acknowledgements

We are grateful to the Science Research Council and Monsanto Chemicals Ltd for financial support. Many helpful discussions with Mr. P. Keating of Monsanto Chemicals Ltd are gratefully acknowledged, and we thank Mr. C. Lam of this Department for the provision of compound (IV).

TABLE 2
Quenching of the excited singlet states of aliphatic ketones

Ketone	Additive	Solvent	$k_Q \times 10^9$ ($m^{-1} s^{-1}$)	$\tau_s \times 10^9$ (s)	Mechanism [10]	Ref.
2-pentanone	biacetyl	cyclohexane	21.1	1.8 [4]	(a)	1
2-butanone	biacetyl	cyclohexane	7.5 (24.7)	6.3 (1.9) [8]	(a)	2
3-pentanone	biacetyl	cyclohexane	7.6 (10.0)	3.7 (2.8) [8]	(a)	2
acetone	biacetyl	cyclohexane	9.4	1.7	(a)	3
4-methyl-2-pentanone	nickel dibutyl-dithiocarbamate	benzene	~ 10 [9]	--	(a)	5
acetone	<i>trans</i> -dicyanoethylene	acetonitrile	2.5	1.7	(d), (c)	6
acetone	<i>cis</i> -diethoxyethylene	acetonitrile	2.0	1.7	(d), (c)	6
2-pentanone	diethylamine	cyclohexane	2.6	1.8	(d)	1
2-pentanone	triethylamine	cyclohexane	1.35	1.8	(d)	1
acetone	1,3-pentadiene	hexane	0.09	2.0	(d), (c)	4
2-pentanone	1,3-pentadiene	hexane	0.04	1.8	(d), (c)	4
3-pentanone	carbon tetrachloride	cyclohexane	0.14	2.8	(d), (c)	7
2-pentanone	carbon tetrachloride	cyclohexane	0.05	1.8	(d), (c)	1
acetone	carbon tetrachloride	cyclohexane	0.04	1.7 [3]	(d), (c)	7
2-pentanone	1-bromohexane	cyclohexane	0.04	1.8	(b)	1

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9 Estimated lifetime 2.0 ns.

10 See text.

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